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THE FINE STRUCTURE OF CERTAIN X-RAY ABSORPTION EDGES

By Katherine Chamberlain

Abstract

X-ray absorption edges for certain elements and compounds.—In a recent paper Coster[1] reports a white line on the long wave-length side of the x-ray absorption edge of some metallic oxides. Evidence is here reported which shows that in each case the white line is the absorption edge for some of the material which had been reduced to the metal by the x-ray beam. Screens were prepared by covering black paper with a thin layer of finely divided metal weighing 2 to 3 mg per cm². (1) *K absorption edges for Ti*(22), *V*(23), *Cr*(24) *and Mn*(25) were found at 2489.5, 2261.9, 2064.9 and 1891.4 x-units. (2) L_{III} *absorption edges for Sn*(50), *Sb*(51) *Te*(52) *and I*(53) are 3146.9, 2291.5, 2847.1 (Coster) and 2712 (Coster). These values are all in good agreement (within less than 1 x-unit) with the positions of Coster's white lines. (3) *In the case of compounds of higher valence*, the white line Coster obtained is therefore due to reduced element. (4) *In the case of sulfides and sulfites*, the secondary absorption edge at 4988 x-units reported by Lindh[3] may likewise be due to traces of sulfate in the screen produced by the action of the x-rays.

Chemical changes produced by x-rays.—Chemical evidence of appreciable reduction of iodic acid and of potassium permanganate is presented, and also of the oxidation of sulfurous acid.

Theory of changes of valence produced by absorption of radiation by elements 22-25 and 50-53 and of consequent chemical changes.—It is proposed that the numerous electron transitions that follow the removal of an electron from its normal orbit by absorption of radiation may occasionally occur in such a way as to result in a change in the general electron configuration such that some of the valence electrons find stable positions farther in, thus resulting in a reduction of valence. Oxidation can also occur when the change in the electron configuration is such as to place an increased number of electrons in the valence group. What makes this proposal seem especially reasonable is that Ti(22), V(23), Cr(24) and Mn(25) occur in a portion of the periodic table in which inner groups are being filled in building new elements while Sn(50), Sb(51), Te(52) and I(53) are found very close to such a group. Bohr thus considers that configurations which place additional electrons in inner groups in this region are stable.

IN a recent article[1] Coster describes the K absorption edges of titanium, vanadium, chromium and manganese and the L_{III} absorption edges of tin, antimony, tellurium and iodine, obtained when various compounds

[1] Coster, Zeits. f. Phys. (July 2, 1924).

were used in the absorbing screens. He found a complicated structure of the absorption edge in each case for the more highly oxidized compounds used. An important feature of the structure was a white line on the long wave-length side of the absorption edge about six or seven x-units from the main edge. It is the purpose of this investigation to inquire further into the significance of this white line. It is not found when the free element or a compound of low valence is used in the absorbing screen.

Coster's data which have to do with the present investigation are given in Tables I and II.

TABLE I

Coster's data for titanium to manganese.

Element	Screen	K absorption edge	White line $K\alpha$	Valence
Titanium(22)	TiO_2	2482.9x	2489.5x	4
	Ti metal	2484.0		
Vanadium(23)	V_2O_5	2256.4	2262.8	5
	$V_2(SO_4)_3$	2256.7		3
Chromium(24)	$Na_2Cr_2O_7$	2059.5	2065.0	6
	K_2CrO_4	2059.1	2065.2	6
	Cr_2O_3	2060.6		3
	$[Cr(NH_3)_6]$ $(NO_3)_3$	2063.8		3
	$CrCl_3$	2063.0		3
Manganese(25)	$KMnO_4$	1886.0	1891.3	7
	$KMnO_4$ (reduced)	1887.5		
	Mn_3O_4	1888.9		
	Manganic acetate	1887.8		3
	$MnSO_4$	1889.2		2

TABLE II

Coster's data for tin to iodine.

Element	Screen	L absorption edge	White line L_{III_a}	Valence
Tin(50)	SnO_2	3140.6x	3147.5x	4
Antimony(51)	$KSbO_3$	2984.1	2990.8	5
	Sb_2O_3	2985.1	2991.1	3
Tellurium(52)	H_2TeO_4	2840.6	2846.6	6
	H_2TeO_3	2842.2	2846.9	4
	Te metal	2847.1		
Iodine(53)	HIO_4	2705.8	2711.3	7
	HIO_3	2707.1	2711.5	5
	KI	2712.2		1
	I	2712		

It will be noted that the wave-length of the absorption edge increases slightly as compounds of lower valence are used in the absorbing screen; also that the white line is, in general, found only with compounds repre-

senting the higher valences and never with the free elements. Moreover, the values for the absorption edges of the free element in the case of both iodine and tellurium fall within a fraction of an x-unit of the white line reported for the oxidized states. This at once suggests that the white line may be the absorption edge of a portion of the material in the absorbing screen that has undergone reduction and that the x-ray beam is the reducing agent.

Experimental Details

The present work was undertaken to investigate the hypothesis that x-rays might reduce part of the highly oxidized compound in passing through the absorbing screen and that the white line reported by Coster might be the simple absorption edge of the reduced portion. The resulting investigation took a two-fold course. In the first place, certain of the compounds used by Coster were exposed to x-rays for a number of hours in the effort to discover whether reduction of the highly oxidized compounds could be demonstrated chemically. In the second place, spectrograms were made of the L_{III} absorption edges of metallic antimony and tin and of the K edges of metallic titanium, vanadium, chromium and manganese to discover whether these would coincide as closely with the white lines obtained with the corresponding oxidized compounds as do the edges for iodine and tellurium in Coster's data.

For the chemical part, the procedure was as follows. Portions of a 25 percent solution of iodic acid in water were introduced into thin walled specimen tubes. These were filled about three fourths full and the neck of the rube rinsed carefully with distilled water before sealing off, to prevent possible reduction of any of the iodic acid by the heat of the blast lamp. One of these tubes also contained about 1 cc of carbon tetrachloride, another, the same amount of chloroform, a third, the same amount of carbon disulphide while several other tubes contained only iodic acid and were broken open and tested with the organic solvents after x-raying. The tubes were placed in a lead covered box containing a Coolidge tube and were exposed to x-rays for about 14 hr with a tension of 35000 volts, a current of 30 milli-amp., and a distance from target to specimen tube of about 5 inches (13 cm). Every sample gave indications of traces of free iodine by imparting a distinct pink coloration to the organic solvent.

The iodic acid was carefully tested with chloroform and found entirely free from iodine before exposure to the x-rays, a precaution that is quite necessary as iodine or iodide in traces frequently contaminate iodic acid. The carbon disulphide was of only technical grade and so not

above suspicion in regard to purity but the chloroform and the carbon tetrachloride had been especially purified for analytical work. Blanks treated exactly as were the other samples except that they were not exposed to the x-rays gave negative tests for iodine. The conclusion is, therefore, that traces of the iodic acid were reduced by the x-rays.

A solution of potassium permanganate, another of the compounds reported by Coster, was next used. This solution was so dilute that the permanganate imparted only a faint pink color to the water. It was placed in a glass stoppered Erlenmeyer flask and exposed to x-rays for two hours. By the end of that time the pink color had entirely disappeared, thus showing undoubted reduction of the permanganate ion.

The remainder of the investigation consisted in getting the L_{III} absorption for antimony and tin and the K absorption for titanium, vanadium, chromium and manganese, using the free metal in each case to make the absorbing screen. All of the spectrograms were made with a Siegbahn spectrograph similar to that used by Coster. The source of high potential was a small transformer giving a maximum potential of 20,000 volts. The potential was controlled by a rheostat in the primary circuit. The rough pump was a General Electric oil pump which was connected both to the x-ray tube and to the spectrograph chamber. A Gaede molecular pump was used as a finishing pump to produce a sufficiently high vacuum in the x-ray tube. Tungsten filaments were used throughout except for titanium when a molybdenum filament was used to prevent possible overlapping of the edge by tungsten lines in the second order.

In most cases the absorbing screens were made by grinding the metals as finely as possible in an agate mortar and then rubbing on pieces of the black paper which is placed by the Eastman Company between pieces of cut film to protect the sensitive emulsion. New screens were made for the duplicate plates in every case where there was any chance that the metal on the screen might have become oxidized by exposure to the air or changed in any other way.

Tin offered special difficulties because its malleability made it impossible to grind it fine, at least at ordinary temperatures. Moreover while it is brittle above 200°C, it proved impossible to get it ground to the necessary degree of fineness at that temperature. The thinnest tinfoil would make an absorbing screen many times as thick as was desired. The method finally used was to precipitate the tin from a slightly acid solution of stannous chloride by placing a sheet of zinc in it. The dark gray sludge thus deposited was scraped off and washed repeatedly with distilled water leaving the tin in flat particles having a metallic luster. The finer particles were separated by swirling in water until all the par-

ticles were in suspension, then allowing the heavier particles to settle out and removing the lighter particles by decantation. This was repeated several times. A Gooch crucible was next fitted with an alundum disk and a piece of the black paper, and a sufficient quantity of the suspension of tin particles in water was filtered through it to cover the black paper with a thin continuous layer of metallic tin. The paper and adhering tin were then dried over a Bunsen flame. In this way an absorbing screen was made which showed no uncovered portions and had a bright metallic luster. The total weight of tin was approximately 3 mg per cm^2. The same method was followed in making one of the absorbing screens used for antimony. It would also have been possible with tellurium but not with chromium, vanadium, manganese or titanium, as these are not reduced to the free metal by zinc. These are, however, sufficiently brittle so that they can be ground to the necessary degree of fineness in an agate mortar and applied to the paper in the dry state.

The weight of absorbing metal was between 2 and 3 mg per cm^2 except one each of Mn and Ti which were 7.5 and 3.6 mg, respectively. In the case of iodine, iodic acid, pure or impure, was used.

Considerable variations in the amount of material on the absorbing screen apparently make little difference in the appearance of the edge. Thicker screens necessitate longer exposures which may have a tendency to obliterate detail by covering it with an excessive amount of secondary radiation. Thin screens are therefore preferable. It would also appear necessary to use samples of the metals that are as pure as possible. The first sample of metallic chromium used was not highly purified and contained a certain amount of slag. Absorbing screens made from this gave spectrograms showing an absorption edge that differed from Coster's white line by several x-units. When a purer sample of metallic chromium was obtained, however, the check was entirely satisfactory.

In certain cases, special precautions had to be taken because the absorption edge was obscured by an emission line. The L_{III} edge of tin falls very close to the $L\alpha$ lines of iodine. In spite of the fact that several plates had been made since any iodine compound had been placed in the tube, these lines both appeared, making the location of the edge somewhat uncertain. It was therefore necessary to scour the interior of the x-ray tube and the target with alundum polishing powder until all discoloration of the brass interior of the tube had been removed. A new focussing cylinder was also put around the filament. After this plates were secured that showed no sign of iodine lines. The titanium edge lies within a few x-units of the $L\beta_2$ line of tungsten in the second order. The tube was

therefore cleaned again and a molybdenum filament used instead of tungsten.

It happened that suitable reference lines fell at convenient places on most plates because of the characteristic radiation of the metals in the x-ray tube. Chromium, manganese, vanadium or titanium salts were not used to obtain reference lines as the $K\beta_2$ lines fall very close to the K absorption edges and there appeared to be danger that faint traces of these lines, if present, might be mistaken for the absorption edges. The only exception was in the case of manganese. Potassium permanganate solution was put on the target and reduced to manganese dioxide by evaporation to dryness in order to use the $K\alpha_1$ line of manganese as a reference line to determine the chromium edge. It was not done, however, until after the manganese absorption had been completed so that there was no danger of obscuring the manganese edge from this source.

Table III gives the values for the white lines reported by Coster on the long wave-length side of the absorption edge for the compounds of higher valence and the simple absorption edges obtained by the writer for the free elements[2] and by Coster for tellurium and iodine.

TABLE III

Absorption edges of free elements.

Element	Screen	White line (Coster)	Absorption edge of free element	Difference Line−edge
Ti	TiO_2	2489.5x	2489.5x	0.0
			2484.0(Coster)	(5.5)
V	V_2O_5	2262.8	2261.9	0.9
Cr	$Na_2Cr_2O_7$	2065.0	2064.9	0.1
Cr	K_2CrO_4	2065.2	2064.9	0.3
Sn	SnO_2	3147.5	3146.9	0.6
Sb	$KSbO_3$	2990.8	2991.5	−0.7
Sb	Sb_2O_3	2991.1	2991.5	−0.4
Mn	$KMnO_4$	1891.3	1891.4	−0.1
Te	H_2TeO_4	2846.6	2847.1 (Coster)	−0.5
Te	H_2TeO_3	2846.9	2847.1 (Coster)	−0.2
I	HIO_4	2711.3	2712 (Coster)	−0.7
I	HIO_3	2711.5	2712 (Coster)	−0.5

In every case, with the exception of Coster's value for titanium, the absorption edge of the free element coincides within the limits of experimental error with the white line. Apparently, Coster's sample of titanium had become oxidized for Lindh reports a value for the titanium edge in

[2] The data for tellurium, iodine, antimony, and tin were reported together with the hypothesis proposed here, in Nature, October 4, 1924. Confirmatory data upon titanium, vanadium, chromium and manganese have appeared in an article by Lindh (Zeits. f. Phys., February 11, 1925). His value for the absorption edge of metallic titanium is 2491.2 x-units.

substantial agreement with that of the present writer.[2] It would therefore seem conclusive that the spectrographic data for all eight elements concerned corroborate the chemical evidence of reduction obtained with iodic acid and potassium permanganate. One more piece of evidence in regard to the origin of the white lines can be offered here. Plates were made of the absorption with iodic acid using in one case a sample of the acid known to be free from the reduced forms of iodine and in the other, a sample that gave a test for contamination with traces of iodide or iodine. Both plates showed the white line but it was clearer on the plate made with the impure acid.

The evidence obtained would indicate that only traces of the material in the absorbing screen are reduced. Thus, we should expect the effect upon the photographic plate to be similar to that produced by a very thin absorbing screen. With such screens practically all the absorption is frequently confined to a very narrow band which gives the appearance of a white line on the plate such as Coster describes.

Certain evidence has been obtained that the x-ray beam can oxidize quadrivalent sulfur in sulfurous acid to the hexavalent form which would indicate that this is at least a contributing cause in the production of the secondary edges which Lindh reports in the neighborhood of 4988 x-units for the lower valence forms of sulfur.

The general plan was to make an acid solution of a soluble sulfite containing a small amount of barium chloride which, in the presence of sulfate, will precipitate barium sulfate, a very insoluble, dense, crystalline precipitate. It proved impossible to secure any sample of sodium sulfite prepared by the manufacturers of chemicals that was not contaminated with considerable quantities of sulfate. This is probably characteristic of all sulfites, and to a considerable extent of sulfides, that they will not be free from traces of sulfate unless special precautions are taken to prepare them in an atmosphere free from oxygen and to keep them from the oxygen of the air during use.

It was therefore decided to prepare a solution of sulfurous acid in water containing a small amount of barium chloride by saturating it with sulphur dioxide and to expose the solution thus formed to the x-ray beam to discover whether any of it would become oxidized to sulphate. The preparation of sulfurous acid free from all traces of sulfate proved rather difficult. The sulfur dioxide procurable in tanks contained sufficient oxygen to oxidize an appreciable amount of the sulphurous acid. The procedure finally adopted was as follows. Bulbs having a capacity of about 50 cc and a very thin wall were blown on one end of glass specimen tubes and the tubes were constricted above the bulb to facili-

tate sealing off after the specimen had been prepared. The whole was fitted with a two hole stopper, a delivery tube leading to the bottom of the bulb, and an outlet tube. Meanwhile, a sulfur dioxide generator had been set up containing about two hundred grams of acid sodium sulfite and about four hundred cubic centimeters of water. Concentrated sulfuric acid could be admitted as required through a dropping funnel. The generator was connected to a water trap, to insure that no sulfuric acid should be carried over, and then to the bulb. Before use, the generator was allowed to operate for some time to be certain that all air was removed. Meanwhile, one of the bulbs was filled with conductivity water, the purest distilled water obtainable, and boiled under a reflux condenser for about fifteen minutes to remove any oxygen that might be dissolved in the water. It was then connected as quickly as possible to the sulfur dioxide generator and sulfur dioxide passed in for about an hour and a half. By the end of this time, the contents of the bulb had cooled to room temperature and were saturated with the gas so the bulb was immediately sealed off in the flame of a blast lamp.

In this way two samples were prepared entirely free from turbidity. They were set aside for about ten hours as a precipitate is sometimes very slow in forming. When no precipitate had formed by the end of this time, however, it seemed conclusive that neither sulfate nor oxidizing agent capable of producing any was present in either bulb.

One was therefore set aside as a blank and the other exposed to the x-ray for about forty milli-ampere hours under a tension of a hundred and ten thousand volts. By the end of this time a small amount of barium sulfate had been precipitated thus demonstrating that traces of the material had become oxidized by the x-ray beam for the bulb that had not been x-rayed remained clear. Later, in order to make the test more conclusive, the other specimen was also exposed to the x-ray beam and a precipitate formed.

Lindh[3] has questioned the real existence of a secondary absorption edge in the case of quadrivalent sulfur because of the readiness with which it undergoes oxidation. The present writer would go a step farther and question whether any of the secondary edges reported by him at a wavelength in the neighborhood of 4988 x-units for divalent and quadrivalent compounds of sulfur are other than the simple absorption edges of hexavalent sulfur. Our experience here would indicate that the principal oxidizing agent is probably the oxygen of the air but the x-ray beam itself is quite evidently a contributing cause.

[3] Siegbahn, Spektroscopie der Röntgenstrahlen, p. 142.

Underlying Theory of This Absorption

It will next be of interest to consider the bearing of these results upon the Bohr theory. While nothing definite has been said by Bohr regarding the valence electrons of these elements, the inference has always been that these are located in the electron groups of highest quantum number, i.e. in those groups representing electron orbits having the greatest major axes. Lewis,[4] Bury,[5] and J. J. Thomson[6] carry this a step farther and suggest that oxidation and reduction changes represent an increase or decrease in the number of electrons in the valence ring by a change in the number of electrons in inner groups. These outer electrons are the electrons that give rise to optical spectra, and require so little energy to eject them from their normal orbits to the periphery of the atom or beyond, that radiation of longer wave-length than that considered here will be required. Therefore, the way in which they are most likely to be removed by x-radiation is by what we may call the indirect method.

The mechanism of the process may be somewhat as follows. Below is the electron arrangement given by Bohr for titanium.

Group	K	L	M	N
Quantum numbers	1_1	$2_1,2_2$	$3_1,3_2,3_3,$	4_1
Number of electrons	2	4,4	4,4,2,	(2)

Since the atomic number of titanium is 22, only four groups of orbits, K, L, M and N, are possible. The energy level diagram shows one K level, three L levels, five M levels and one N level.

Suppose that radiation of the frequency required to eject an electron from the K orbit outside the atom is allowed to fall upon a titanium absorbing screen. The possible transitions, taking proper account of the Selection Principle, by means of which the vacant place may be filled again, are as follows. An electron might fall from the M_3 level to the K giving rise to radiation of the frequency designated as the $K\beta_1$ line. The vacant place in the M_3 level might then be filled by an electron from the N level and the electron originally ejected from the K to the periphery might fall back into the vacant place in the N. This is a typical case only, for a variety of transitions are possible, but the point is that any such phenomenon involves numerous transitions between the various electron orbits. It would therefore seem possible that, as a result of all these transitions, in certain cases a sufficient alteration of the atomic configuration might occur so that the possible number of electrons in groups of lower quantum number might increase, thus providing for more

[4] Lewis, Jour. Am. Chem. Soc. **38**, 770 (1916).
[5] Bury, Jour. Am. Chem. Soc. **43**, 1602 (1921).
[6] J. J. Thomson, The Electron in Chemistry, p. 96-99 (1923).

electrons in such groups and a corresponding reduction in the number of electrons in the valence group. This would seem to be a reasonable extension of Bohr's hypothesis regarding the formation of the rare earth group.

It will be recalled that he accounts for the formation of this group by the hypothesis that when electrons are added to compensate for the increased nuclear charge in passing from element to element, they are inserted into groups of lower quantum number. Thus, the most stable position open to the last added electron is at times in an electron group of lower quantum number than that available for those added just previously. In other words, at certain points in the up-building of the elements, electrons begin to be inserted again into groups of lower quantum number that had previously been in a state of temporary completion. If this occurs in the building up of new elements, it seems reasonable to inquire whether it might not occur also in a particular element when x-radiation falls upon it and produces numerous electron transitions in its atoms. Some of these transitions may produce a change in the configuration of certain orbits that would provide stable positions for part of the valence electrons in orbits of lower quantum number, thus resulting in a reduction of valence. Moreover, if some of the valence electrons were moved to positions in groups of lower quantum number, they would exert a shielding effect upon the outer electrons with a consequent slight reduction in the energy of these outer orbits. As a result, it would be expected that the different absorption edges would represent slightly less energy when the element exists in its lower valence forms; i.e., the wave-length of the edge would be slightly longer for a compound of low valence than for one of high. It will be noted that this is exactly what is found when the absorption edges are determined experimentally for the different valence forms of the same element.

If the mechanism of the process is as proposed here, oxidation as well as reduction by the x-ray beam may be considered possible. In fact, even if these changes of electron configuration occur only temporarily, they may be expected to produce an effect upon the absorption edge. Oxidation effects produced in this way would probably not be visible in many cases for the edge of the oxidized form would fall on the short wave-length side of the main edge; i.e. in that region in which absorption is already at a maximum, so that it would not be likely to be visible except in the case of those elements whose absorption edges for the various valence forms differ from each other by a number of x-units. Sulfur is an element whose absorption edges meet this requirement and

Lindh's data[7] showing multiple edges in the case of certain of its compounds exhibit rather greater agreement in wave-length between the secondary edges of lower valence compounds and the principal edges of those of higher valence than seems reasonable to attribute to chance. At least it seems reasonable to consider that the first secondary edge reported by Lindh[3] for various sulfides and sulfites is due to the presence of traces of hexavalent sulfur in the absorbing screens, as compounds of these kinds are slowly oxidized by exposure to the oxygen of the air. Moreover, sulfides and sulfites that are entirely free from traces of sulfate are almost unknown. It has also been shown that the x-ray beam itself can bring about oxidation of a portion of the material in the absorbing screen.

Attention might be called to the fact that titanium, vanadium, chromium, and manganese occur in a region in the periodic system in which Bohr proposes that the added electrons in building new elements are being inserted into inner groups. While it is true that the tin, antimony, tellurium, iodine group is built up by inserting electrons in the groups of highest quantum number rather than in inner positions, it seems significant to note that they come only three elements below the rare earth group and here, again, electrons begin to be inserted into inner groups. Thus, we find that both of these groups of elements that are capable of oxidation and reduction either fall in a portion of the periodic table in which electrons are being inserted into inner quantum groups or very close to such a portion. This would seem to make it extremely probable that electron shifts from outer to inner groups or vice versa may take place here in a particular element and that these shifts would result in a change of valence.

Exactly to what extent valence changes in the absorbing screen can account for the fine structure of absorption edges, it will be impossible to say until more data are available. Evidently, however, such changes must be taken into account in the interpretation of all absorption edges involving elements that are capable of oxidation and reduction and they may explain much that has previously been obscure regarding fine structure. Moreover, it may prove possible to reverse the process and interpret chemical valence in the light of the Bohr theory by a study of the absorption edges of elements that are capable of oxidation and reduction. Last, a systematic study of x-rays as an oxidizing or reducing agent for inorganic compounds may give the key to the solution of that vastly more difficult problem of what occurs in the human body when x-rays are used as a therapeutic agent.

[7] Lindh, Dissertation, Lund (1923).

In conclusion, I should like to express my thanks to Dr. George A. Lindsay, of the University of Michigan, for the use of a Siegbahn spectrograph and for valuable criticism during the progress of this work, to Mr. William Fink and Mr. James Kassner for helpful suggestions in regard to the chemical part of this investigation, and to Dr. Coster for his interest in my preliminary report and for the encouragement he offered to carry the work farther.

PHYSICS LABORATORY,
UNIVERSITY OF MICHIGAN,
May 27, 1925.

CHARACTERISTICS AND SPECTRA OF LOW VOLTAGE ARCS IN H_2, N_2 AND IN MIXTURES OF H_2 WITH Hg AND N_2

By C. T. Kwei

Abstract

I. *Arc characteristics.*—The tube used was a spherical bulb containing a Ni disk electrode and a W spiral filament and provided with a quartz window and an appendix in which could be placed liquid Hg. By applying corrections for filament drop and for initial velocities, approximately measured by use of a high resistance voltmeter, remarkably consistent values for the breaking voltages were obtained. (1) *With pure hydrogen*, there were no oscillations; the arc broke at the *ionization potential* 16.2 volts; and by plotting the 2/3 power of the current as a function of the voltage, the ionization potential of the atom was located at 13.7 volts. These voltages are subject to a correction of about −0.5 volt for contact potential difference. (2) *With pure nitrogen*, the breaking potential 16.2 is not the ionization potential since oscillations occur below 16.9, the actual ionization potential, as shown by oscillograph observations. (3) *In mixtures of H_2 with Hg*, a careful study was made for pressures of H_2 from 0.1 to 3.0 mm, and with the Hg appendix at room temperature and at 100°C. Below a critical pressure of H_2, depending on the Hg pressure, oscillations of one or two types occurred. With the filament not too hot, 0.8 mm of H_2 and Hg at 20°C, two arcing and two breaking potentials were observed. The curve as far as the second arcing potential, was reversible. The difference between the two arcing potentials is about 10.4 volts, the ionization potential of Hg. When a single breaking potential was observed, it decreased with the pressure of H_2, being approximately a weighted mean of the breaking potentials in the pure gases. (4) *Mixtures of H_2 and N_2* behaved similarly to the mixtures with Hg. The breaking potential reached a minimum value for equal pressures of H_2 and N_2. Under some circumstances two arcing potentials (3 volts apart) and two breaking potentials were observed. Oscillations of two types were likewise obtained. A break was observed at 22.7 volts which seems to be a critical potential for N_2.

II. *Spectroscopic observations.*—(1) *In H_2*, the Balmer lines and secondary spectrum appeared together. (2) *In mixtures of H_2 with Hg*, the Hg lines ($2p-ms$) and ($2p-md$) were weak below the second arcing potential and much intensified above it, while the secondary H_2 spectrum and other bands were weakened or disappeared. (3) *In mixtures of H_2 with N_2*, evidence was obtained which indicates that the *ultraviolet band of ammonia*, associated with the 22.5 volt critical potential, is due to a molecule NH_x, where x is probably 3, and that the *Schuster band* is emitted only in the presence of oxygen and is due to a molecule $N_xH_yO_z$, possibly NH_4OH. This band was observed only at voltages higher than the critical voltage for "active nitrogen," 70.

Introduction

RECENT experiments in low-voltage arcs have yielded a number of interesting, though in some cases puzzling, results. It is now known that arcs may be maintained in gases and vapors at voltages as low as

their ionizing potentials and in certain monatomic gases as low as their radiating potentials. The latter phenomenon is generally accounted for by the theory[1] that cumulative action is largely responsible for the ionization of partially ionized or excited atoms. Cases were also observed in which arcs were maintained at voltages too far below the radiating potentials to be accounted for by the velocity distribution of electrons. These were found to be due to oscillations in the arc such that the maximum voltage peaks would always be higher than the radiating potentials. This fact was independently discovered by Bär, v. Laue, and Meyer[2] and Eckart and Compton.[3] The last mentioned authors[4] were also able to maintain abnormal low voltage arcs in argon, helium and mercury vapor without oscillations and demonstrated by means of an exploring electrode that the cathode drop was invariably near the radiating potential and that the abnormal low voltage was due to a reverse field between the cathode drop and the anode, which they attribute to the diffusion of electrons, maintained by concentration gradient, against an electric field.

Duffendack[5] studied the low voltage arcs and the associated spectra in several diatomic gases—hydrogen, nitrogen, and iodine. He was able to determine the ionization potential for atomic hydrogen by maintaining an arc in the gas dissociated by means of an electrically heated tungsten tube furnace, and the value thus determined was in good agreement with Bohr's predictions. Similar results were obtained in iodine. In nitrogen, the dissociation was not appreciable when the arc struck, but above 70 volts the conductivity of the arc rapidly increased, and a brilliant flare appeared which Duffendack identified with the formation of "active nitrogen" as described by Strutt.[6] More recently Richardson and Tanaka[7] studied the striking and breaking potentials in hydrogen and concluded, as did Duffendack, that the breaking potential was a critical potential for the gas, but they differed from him in attributing it, from spectroscopic considerations, to the ionization of the hydrogen molecule as against dissociation plus ionization of one of the atoms. A recent important experiment by Smyth,[8] in which the positive ray method was employed in analyzing the ions formed in the hydrogen discharge,

[1] K. T. Compton, Phys. Rev. **20**, 283 (1922); Van der Bijl, ibid, **10**, 645 (1917).
[2] Bär. v. Laue and Meyer, Zeits. f. Phys. **20**, 82 (1923).
[3] Eckart and Compton, Phys. Rev. **24**, 97 (1924).
[4] Eckart and Compton, Phys. Rev. **25**, 139 (1925).
[5] Duffendack, Phys. Rev. **20**, 665 (1922).
[6] Strutt, Roy. Soc. Proc. **85A**, 219 (1911) et seq.
[7] Richardson and Tanaka, Roy. Soc. Proc. **106A**, 640 (1924).
[8] Smyth, Roy. Soc. Proc. **105A**, 116 (1924); Phys. Rev. **25**, 452 (1925).

seems to have decided definitely in favor of the ionization of the hydrogen molecule.

The work on low voltage arcs has now been extended to mixtures of gases and has already proven itself a promising method for investigating certain chemical properties of elements, such as combination and dissociation. In particular, although the synthesis of ammonia from hydrogen and nitrogen by electrical excitation was discovered over fifty years ago,[9] only a beginning toward analyzing the process has been made through the work of Andersen[10] and of Storch and Olson.[11] These authors detected the formation of ammonia in low voltage arcs in mixtures of hydrogen and nitrogen and by noting the rate of reaction concluded that the formation of ammonia in any appreciable amount occurred only after the arc was struck. Thus the critical potentials of the constituent gases and the rates of reaction as well as the spectra observed at various voltages afford several co-ordinating lines of approach towards a clearer understanding of chemical reaction.

To attack a slightly different problem, Duffendack and Compton[12] studied low voltage arcs in mixtures of hydrogen and mercury vapor and found that the dissociation of the hydrogen molecules in mercury arcs increased ten times in the 5 volt arc and three times in the 10 volt arc as a result of the presence of the mercury. This increase was explained as being due to "collisions of the second kind," in which the hydrogen molecules received the requisite energy of dissociation from excited mercury atoms in the $2p$ states. In mixtures of nitrogen and mercury vapor, the dissociation (or perhaps activation) was found to be only one tenth as large.

Aside from the possibilities of studying combination and dissociation, the low voltage arc offers a convenient method for exciting spectra, for it removes certain objections usually connected with the flame or high voltage excitation. Thus the flame is incapable of excluding impurities present in it and may not furnish enough energy for excitation, and the high voltage discharge is likely to cause dissociation and release of occluded gases from the electrodes and walls. The purpose of our experiment then is to correlate the arcing characteristics in mixtures of gases with the spectra observable at various potentials.

[9] W. F. Donkin, Roy. Soc. Proc. **21,** 281 (1873).
[10] Andersen, Zeits. f. Physik, **10,** 64 (1922).
[11] Storch and Olson, Jour. Am. Chem. Soc. **45,** 1605 (1923).
[12] Duffendack and Compton, Phys. Rev. **23,** 583 (1924).

Apparatus and Method

The apparatus consisted of a simple two-electrode discharge tube in the form of a spherical bulb 9 cm in diameter. The anode was a round nickel plate about 3 cm in diameter. The cathode was a hot filament made of 15 mil (.38 mm) tungsten wire wound closely in the middle into a helical spring of three turns. The electrodes were welded to tungsten leads which were sealed into ground glass stoppers and these in turn were sealed to the experimental tube by means of hard DeKhotinsky cement which was disposed so as to reduce to a minimum the presence of cement vapor in the tube. Vertically attached to the bottom of the bulb was a small glass appendix. When a mixture of mercury vapor and another gas was desired, this was filled 4 or 5 mm deep with mercury and could be heated up to the boiling point of water by immersing the tube in a water bath.

For spectroscopic observations, a side tube 15 cm in length and 1.7 cm in diameter was horizontally attached to one side of the bulb and a quartz window was fastened to it at the end. The light from any region between the target and filament or behind the filament was brought to a focus on the spectrometer slit by means of a quartz lens. The spectrum was observed with a direct reading constant deviation spectrometer for the visible region and photographs were taken with a small Hilger quartz spectrograph for the ultraviolet region.

The filament was heated through an adjustable carbon resistance by means of storage batteries. The voltage impressed on the plate was tapped from a potentiometer arrangement which was connected at will, by means of a double-pole double-throw reversing switch, to either the positive or negative side of the filament. It was found that the mean value of a critical potential from readings at the two positions was not always equal to the voltmeter reading plus or minus one half the filament drop of potential. In this experiment, only the mean values were taken.

The hydrogen and oxygen used in this experiment were prepared by electrolysis of dilute sulfuric acid. The nitrogen was prepared by dropping liquid bromine into concentrated ammonia, and was then made to pass through a wash bottle containing dilute ammonia and a second wash bottle containing dilute sulfuric acid to remove traces of bromine and ammonia, respectively. Each of these gases was stored in a drying tube for at least 24 hours over phosphorus pentoxide before it was admitted through a stop cock and a mercury cut off into a large reservoir 120 cm high and about 30 cm^2 in cross section. The large volume of the reservoir proved to be very convenient for adjustments at low pressures and re-

duced the rate of pressure change due to "clean-up." Another mercury cut off was inserted between the reservoir and two liquid air traps connected in series leading to the experimental bulb so that a small change in the pressure of the gas would be sensitively noticed by cutting off the large volume. The system was evacuated by means of a mercury diffusion pump backed by a high vacuum oil pump. For the identification of the ultraviolet and Schuster bands of ammonia, this gas was generated by evaporating a strong ammonia solution and the gas was dried by storing it over potassium hydroxide sticks.

Before a new gas was tried, the experimental bulb was usually baked for three or four hours in an electric furnace at a temperature between 300° and 350°C. The traps were constantly immersed in liquid air to condense any moisture or mercury vapor in the system, except when ammonia was used.

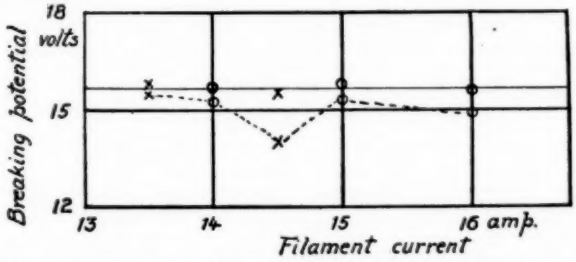

Fig. 1. Breaking potential in a mixture of N_2 and H_2. Pressure for crosses was 0.8 mm, for circles 0.5 mm. The lower curve is uncorrected for "initial voltmeter" reading.

In agreement with Richardson and Tanaka[7] the writer found that when the filament current remained constant, the breaking potential of the arcs tended toward a minimum at a definite pressure. The minimum voltage was found at a pressure of about 0.5 mm, and the breaking voltages did not exceed this minimum by more than 0.25 volt between pressures 0.2 and 1.0 mm. The excess voltage at low pressures must be due to an insufficient supply of molecules to be ionized and at high pressures to energy losses which do not contribute to ionization. It was also found that with the increase of filament temperature, the breaking potential tended to diminish, probably due to the increase in initial velocities of the electrons. To correct this effect to a first approximation, a Cambridge and Paul universal test set was used as a high resistance voltmeter to measure the potential difference of the electrodes, acquired as a result of the thermionic emission only, before the impressed voltage was applied. When this reading, designated as the "initial voltmeter reading" was added, the various breaking potentials became much more uniform. Fig. 1 illustrates this point. This correction was made for all determina-

tions except those of a second arcing potential, where the variation of the second jump exceeded the value of the correction.

Since some of the apparent current-voltage characteristics were due to oscillations in the arc, these were detected and studied by use of a Western Electric cathode ray oscillograph, which was used so as to measure current and voltage along mutually perpendicular axes on the fluorescent screen.

Arc Characteristics in Hydrogen and in Mixtures of Mercury Vapor and Hydrogen

Before the mixtures were tried, preliminary runs were made with hydrogen. The voltage-current characteristics were found to be very

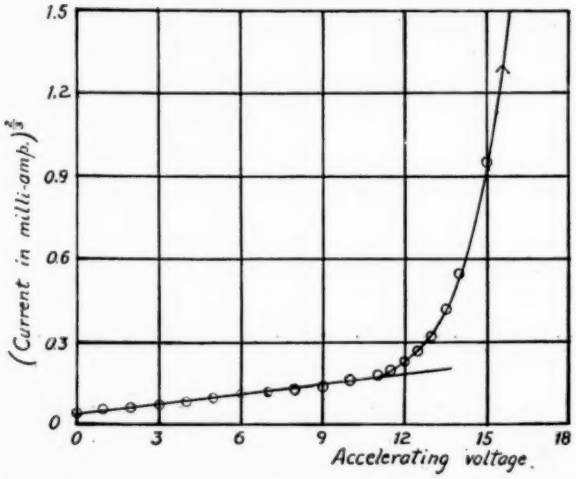

Fig. 2. Ionization potential of atomic hydrogen. Value observed 11.0 volts; with connections reversed 15.0 volts; mean value 13.0 volts. Initial voltmeter reading 0.5 volt. Corrected value 13.5 volts.

similar to those observed by Duffendack: 1. The potential of the break was always lower than the striking potential, usually by several volts, the difference being greater at higher pressures. In each case the varying factor was the striking potential while the breaking potential remained practically constant at 16 volts. 2. The breaking potential, pressure remaining the same, became slightly less with increasing filament temperature. This effect was corrected for by taking the "initial voltmeter" reading as described in the preceding section.

Limiting the pressure range to 0.4 to 1.0 mm, the corrected breaking potential as an average of sixteen runs was found to be $16.17 \pm .05$ volts. An independent series of eleven runs was made several months later with different electrodes and the average was found to be $16.23 \pm .03$ volts.

Both of these results are in excellent agreement with Duffendack's value of $16.18 \pm .05$ volts. We shall take 16.2 as our experimental value for the ionization potential of the hydrogen molecule.

It was suspected that thermal dissociation due to the filament might furnish enough atoms to make the effect of atomic ionization detectable. Graphs were plotted on a magnified scale to see if the increase of current with voltage deviated from the $i \propto V^{3/2}$ relationship. The point of departure of the curve from a straight line was taken as the value for the ionization potential for the hydrogen atom. Six graphs similar to Fig. 2 were plotted and the average potential came out to be $13.67 \pm .14$ volts, which is near the 13.5 volt value calculated from the limit of the Lyman series.

When mercury was introduced into the appended tube, as described in the preceding section, and immersed in a water bath at room temperature, it was found that the *breaking potential* was systematically reduced in proportion as the relative amount of hydrogen in the presence of mercury vapor was diminished. The first two columns of Table I contain the experimental data.

TABLE I

Arc in mixture of hydrogen with Hg vapor at room temperature

Pressure of hydrogen	Breaking potential (observed)	(calculated)
1.1 mm	16.34 volts	15.8 volts
.7	15.90	15.6
.35	15.22	15.1
.25	14.61	14.7
.15	14.27	14.2
.09	13.30	13.5

When the filament temperature was not too high, it was possible, in the mixture of hydrogen and mercury vapor maintained at room temperature, to locate a second striking potential when the pressure of hydrogen was at or below 1 mm. This is shown in Fig. 3. Very often when the voltage was lowered there were two breaking potentials, the first one being a volt or so lower than the second. Table II contains a summary of the readings.

It is seen that the two arcing and breaking potentials were observable at higher hydrogen concentrations. When the curve was retraced before the second arcing potential was reached, there was a marked approach to reversibility which is a prominent attribute of arcs with oscillations, as will be shown below. This is shown in Fig. 4. The breaking point here corresponds to the one observed in pure hydrogen.

Interpretation of current-voltage relations in mercury-hydrogen mixtures. It is rather surprising that two distinct breaks were not observed corresponding to the ionization potential for the hydrogen molecule at 16.2

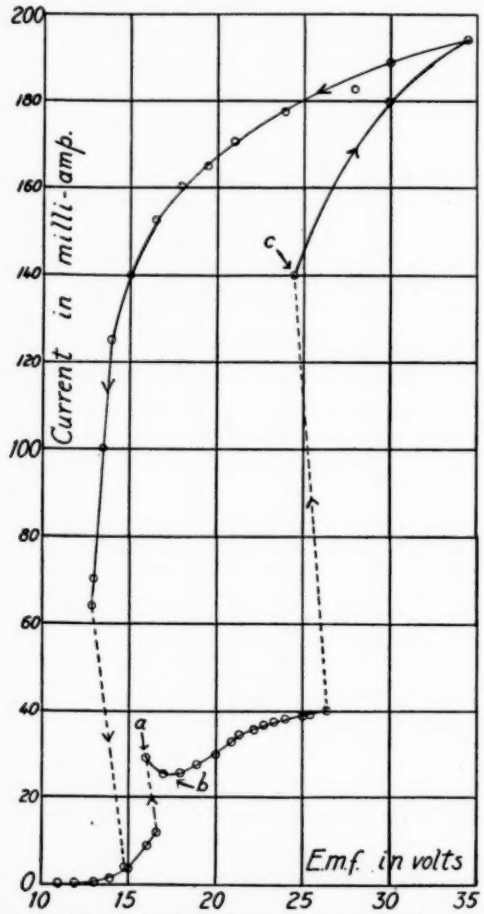

Fig. 3. Showing two striking potentials. Mercury appendix kept at room temperature. Pressure of hydrogen 0.75 mm. Readings uncorrected for filament drop.

TABLE II

Arc in mixture of hydrogen and mercury vapor, with mercury appendix at room temperature

Pressure of hydrogen	Striking potential		Breaking potential	
	1st	2nd	1st	2nd
mm	volts	volts	volts	volts
0.9	19.5	28.6	15.3	16.9
0.8	18.9	28.2	15.0	16.1
0.7	25.5		15.1	
0.5	19.1		15.3	
0.35	19.7		15.2	

volts and for the mercury atom at 10.4 volts. An examination of the data suggests that the potential observed may be a weighted mean of the two critical potentials, depending upon the relative effectiveness of each constituent in neutralizing space charge around the filament. This

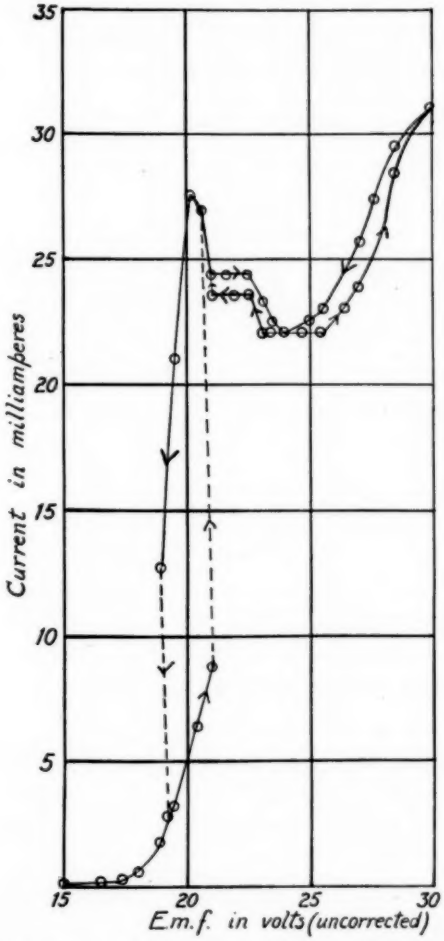

Fig. 4. Arc characteristics in mixture of mercury and hydrogen, when process was reversed before reaching the second striking potential.

depends upon the number of molecules of each gas present to be ionized, as well as the effective duration of the respective types of positive ions in the region of the space charge around the cathode.[13]

Let N_1, N_2 be the concentrations of mercury atoms and hydrogen molecules, respectively; T_1, T_2 be the average durations of the respective

[13] For theory of the low voltage arc consult K. T. Compton, Phys. Rev. **20**, 183 (1922).

ions; V_1, V_2 their respective ionizing potentials. Then the weighted mean breaking voltages may be taken as

$$V'=\frac{N_1T_1V_1+N_2T_2V_2}{N_1T_1+N_2T_2}=\frac{T_1V_1+(N_2/N_1)T_2V_2}{T_1+(N_2/N_1)T_2}. \tag{1}$$

Now in an electric field of given potential drop, the hydrogen and the mercury ions will move in such a way that

$$\tfrac{1}{2}M_1v_1^2=\tfrac{1}{2}M_2v_2^2, \tag{2}$$

where M_1v_1 and M_2v_2 refer to the mass and velocity of the mercury and hydrogen ions respectively. Therefore,

$$v_1/v_2=\sqrt{M_2/M_1}=T_2/T_1. \tag{3}$$

In the present case $M_1=200.6$ and $M_2=2.016$. Thus $T_1=10T_2$ approximately.

The ratio N_1/N_2 may be found by taking the ratio p_1/p_2 where p_1 represents the partial pressure of mercury vapor and p_2 that of hydrogen. Hence Eq. (1) may be written in this form

$$V'=\frac{10V_1+(p_2/p_1)V_2}{10+(p_2/p_1)}. \tag{4}$$

The values of V' thus calculated are tabulated in column 3 of Table I. The assumed pressure was .008 mm, which is the vapor pressure of mercury at 46°C. This is about 20° higher than the temperature of the water bath in which the mercury was immersed, but is a reasonable value owing to the heat from the filament.

The calculated values are in fairly good agreement with the observed values, except for higher pressures. This is perhaps due to the effect of increased hydrogen in reducing the amount by which the mercury is warmed by the filament.

Oscillograph study. An oscillograph study of the current-voltage characteristics further confirmed the reasonableness of this view. It was observed that when oscillations appeared in the arc of the mixture, there was a tendency for the arc to stay at either the maximum or minimum points for the longer time, depending upon the relative amount of hydrogen present. In general when the pressure of hydrogen was reduced, the oscillations extended in the direction of the lower voltage.

When hydrogen alone was used, no oscillations were observed under varying conditions of pressure and filament temperature and the arc was found to break at 16.2 volts.

When mercury in the trap was kept at room temperature (the actual temperature in the tube as we have explained must have been higher), the arcing characteristics for pressure higher than 0.8 mm were similar to those in pure hydrogen. Below this pressure there were two distinct types of oscillations, one being of greater amplitude and at a higher voltage than the other. Fig. 5A is a schematic diagram illustrating the behavior. It will be noted that the process was reversible.

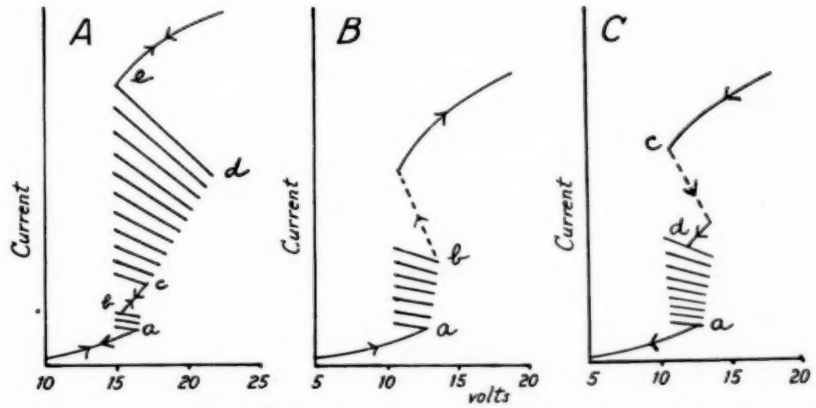

Fig. 5. Types of oscillations in mixtures of mercury vapor and hydrogen.
5A: *a* at 16.5, *b* at 15.3, *c* at 17.2, *d* at 21.8, *e* at 14.5 volts;
5B: *a* at 13.0, *b* at 13.3 volts;
5C: *a* at 13.0, *c* at 10.8, *d* at 12.0 volts.

The oscillations were more difficult to excite when the mercury trap was immersed in the water bath at the boiling point of water (actual temperature much lower of course in the tube owing to condensation in liquid air traps and cool parts of the tube). No oscillations were observed until the hydrogen pressure was reduced to 0.4 mm. The results are tabulated in Table III. The results in the fourth column were calculated

TABLE III

Arc in mixture of hydrogen with mercury vapor with mercury appendix at 100°C

Pressure of hydrogen	Striking potential	Breaking potential (observed)	(calculated)
3.0 mm	33.1 volts	16.7 volts	15.5 volts
2.1	31.0	16.0	15.3
1.5	27.3	15.0	15.0
1.1	25.1	14.6	14.7
0.8	20.7	14.1	14.3
0.4		oscillations set in	

from Eq. (4), assuming the pressure of mercury vapor to be 0.4 mm at an assumed bulb temperature of 65°C. Here the larger discrepancies at high

pressures may be attributed to the fact that these pressures are beyond the range in which the arc breaks at the minimum voltage.

Figures 5B and 5C show the type of oscillations which set in at about 0.4 mm with this concentration of mercury vapor. The amplitude of oscillations was evidently larger than in the case of lower concentration and the type that previously appeared at a higher voltage was not present.

In order to account for the peculiar behavior of the oscillations with the two pressures of mercury vapor, let us assume the following cycle of operations. The arc in the mixture was struck only after a sufficient number of hydrogen molecules was ionized under the unfavorable conditions of negative space charge around the filament, since the number of mercury atoms present was always a small fraction of the mixed gases. The increased arc current would now ionize a number of mercury atoms and excite a sufficient number that would dissociate hydrogen molecules by means of "collisions of the second kind," the evidence of which is amply given by the experiments of Cario and Franck,[14] Duffendack and Compton,[12] and Compton and Turner,[15] as well as by the spectroscopic data in this experiment to be presented in the sequel. Both of these effects would further increase the arc current, as was observed. When the voltage was lowered, there might be a sufficient number of positive ions of mercury and of atomic hydrogen effectively to maintain the arc at a lower voltage than in pure hydrogen. However, if these atomic ions could not be sufficiently replaced, as probably would be the case with lower pressure of mercury vapor and therefore less dissociation of the hydrogen molecules, then the current would tend to diminish until the accompanying rise in voltage was enough to again ionize the hydrogen molecules and the cycle was repeated in the form of oscillations.

Spectroscopic Observations on Mercury Vapor and Hydrogen

In pure hydrogen the Balmer lines and the secondary spectrum always appeared together, as soon as the arc was struck, with the Balmer lines more intense than the secondary spectrum. This is due, judging by Smyth's conclusions, to the ionization of the hydrogen atoms formed as a result of secondary collisions. Richardson and Tanaka used lower pressures (.2 mm) than those the writer employed (0.4 to 3.0 mm) and succeeded in actually observing the relative absence of the Balmer lines in the region of bluish glow in front of the anode on the side nearest the

[14] Cario and Franck, Zeits. f. Phys. **11**, 161 (1922).
[15] Compton and Turner, Phil. Mag. **48**, 360 (1924).

cathode. On the anode side the glow was pink and the Balmer lines were relatively more intense.

In mixtures of mercury vapor and hydrogen, the mercury lines and the Balmer series lines were very much enhanced relative to the secondary spectrum after passing the second arcing potential. We shall further examine this in detail. On the return path of voltage change the mercury as well as the hydrogen lines were visible above the upper break. Only the hydrogen spectrum was observable between the upper and lower breaks. Hg line 5461 showed this effect in a most striking manner. When there was only one striking and one breaking potential, the mercury and the hydrogen lines appeared and disappeared together.

Photographs were taken with the type of arc shown in Fig. 3 at the first and second arcing potentials and at the lowest current point between the two. We shall designate these points *a*, *c*, and *b* respectively. The result of examining the photographs may be summarized thus:

1. The mercury lines 5461, 4358, and 4047 were very faint at *a*, not found at *b*, and very much intensified at *c*.

2. The mercury lines 3650, 3132, 3022, 2967, 2803, 2652, and 2537 were more reduced in intensity relative to the rest of the spectrum at *b* compared with the lines at *a*. They were also very much intensified above the higher break.

3. A number of additional Hg lines including 3367, 3352 and 3343 appeared above the higher break.

4. Most of the secondary spectrum lines were reduced in intensity above the higher break.

5. Bands, probably mercury hydride, at 3572, 3531, 3154 were present at *a* and *b* but disappeared at *c*.

6. A band at 3388 was found at *a* and *b* and disappeared at *c*.

One conclusion seems to be unavoidable from these facts, that between the first and second breaks hydrogen molecules were dissociated into atoms. It is significant to note also that the $2p$-ms lines 5461, 4358, 4047 were absent and the $2p$-md lines 3132, 3126, 2967, 3022, 2562 and the $1S$-$2p$ line 2537 were greatly reduced in intensity at *b*, the lowest current point between the two arcing potentials. It seems reasonable to suppose that excited mercury atoms in the $2p$ states lost their energy through impact with hydrogen molecules in dissociating them into atoms, as the reduced intensity of the line 2537 would imply that instead of radiating in returning from the $2p$ state to the normal orbit, the energy of the electrons was absorbed by "collisions of the second kind." Further, it is probable that very few of the mercury atoms were ionized or excited to a higher level than the $2p$ state owing to a large probability of losing

their energy in this state. This very probably accounts for the reduced intensity of lines corresponding to transitions from the s or d states to the $2p$ states.

In this connection it may be suggested that the two reproducible points of discontinuity above the break of Fig. 4 are probably significant of the process of interchange of energy between the hydrogen and mercury vapor, which is proved by the spectra. No very satisfactory interpretation of them has, however, been made.

The relative intensification of the entire mercury spectrum above the upper break lends further support to our assumption that the mercury atoms were increasingly ionized at this point. From Fig. 3 it will be seen that the difference between the two arcing potentials happened to be exactly 10.4 volts, the ionization potential of mercury atoms. Five independent trials gave about the same value for this difference.

The bands observed at a and b are probably mercury hydride bands. They were not observed by Compton and Turner in the positive columns, and the bands observed by them were not detected by the writer; but the origin of the bands in this experiment arose from a region more similar to negative glow than to positive column.

A comparison of the particular lines of the secondary spectrum which were present in a mixture of mercury vapor and hydrogen at the first arcing potential (see Fig. 3) but disappeared at the higher arcing potential leads to the following results. The lines enclosed in brackets were observed after both breaks whereas those without brackets were visible between the two breaks but not above the higher one. 5014, 4930, (4782), 4724, 4684, (4633), (4581), 4555, 4525, 4492, 4449, (4413), (4304), 4254, (4205), (4178), (4158), (4133), 4099, (4064), 3991, 3944, (3890), (3873), (3861), 3804.

This classification has been compared with those based on Zeeman effect, pressure effect, Stark effect and admixture with helium. Unfortunately most of these classifications have not been extensive enough to give a very thorough comparison. In general it may be said that there is no striking agreement between any two of them, a result which emphasizes our ignorance regarding the real origin of the hydrogen secondary spectrum. Unfortunately, the writer did not extend this study to the lines between 5000 and 6400.

When this experiment was in progress, Duffendack published his findings in a similar experiment.[16] He found that practically the entire secondary hydrogen spectrum appeared in full intensity at 15 volts in pure hydrogen and at 14 volts in a mixture of mercury vapor and hydro-

[16] Duffendack, Astrophys. Jour. **60**, 122 (1924).

gen, and concluded that the spectrum must be due to the neutral molecule, as the potential is distinctly below 16 volts. The writer, while agreeing with the findings of his experiment, is unable to concur in the necessity for his interpretation. Duffendack did not take into consideration initial velocity distribution which amounted in the present experiment to as much as one and one half volts for hot filament temperatures as shown in the "initial voltmeter reading." When this correction is made, the result in pure hydrogen can be adequately explained as being due to the ionization of the molecule. When mercury vapor was present, the increased thermionic current involves an increase in the number of high velocity electrons in the same proportion, and the ionization of the hydrogen molecules apparently can be accomplished at a lower weighted mean voltage. Duffendack's observations with respect to the lowering of the breaking potentials in the arcs of the mixtures are in perfect agreement with our results.

Arc Characteristics in Mixtures of Nitrogen and Hydrogen

Preliminary runs in nitrogen alone confirmed Duffendack's[17] conclusion that the arc broke at about 16 volts, which Smyth by his positive ray experiments[18] has conclusively shown to refer to the ionization potential of the nitrogen molecule. It was found that for maintaining a given thermionic current, the filament need not be as hot as in the case of hydrogen, and the voltage current curve was more nearly reversible. Taking the average of eight runs, the breaking potential of the nitrogen arc was found to be $16.18 \pm .05$ volts, which is in excellent agreement with Duffendack's value at 16.17 volts.

There is considerable disagreement among the values reported by various investigators for the ionizing potential of nitrogen,[19] ranging between 15.8 and 18 volts. If the breaking voltage for the arc and the ionizing potential of the gas are identical, both Duffendack's and the present results *seem* to place the potential at 16.2 volts, so that within the errors of experiment the ionization potentials for the hydrogen and for the nitrogen molecules seem to be indistinguishable from each other.

The above result is however quite misleading, for when the arcing characteristics were studied by means of the oscillograph, it was found that the lowest voltage at which the arc could be maintained *without oscillations* was 16.9. Below this voltage oscillations set in with an amplitude of about two volts extending in the direction of lower voltage.

[17] Duffendack, Phys. Rev. **20**, 665 (1922).
[18] Smyth, Roy. Soc. Proc. **A104**, 121 (1923).
[19] Consult for instance Duffendack's table, Phys. Rev. **20**, 681 (1922).

This accounts for our low value in nitrogen, since the voltmeter reading corresponded to the weighted mean of the high and low peaks of the oscillations.

As in the case of the oscillations in the mixture of mercury vapor and hydrogen, the process of making and breaking the arc was nearly reversible. Fig. 6 is a schematic diagram representing the observations. The oscillations started in at about 17.5 volts or above until the current reached a suitable value and then the arc was maintained at 16.9 volts or above without oscillations. When the voltage was gradually diminished, the oscillations again appeared at 16.9 volts. From eight inde-

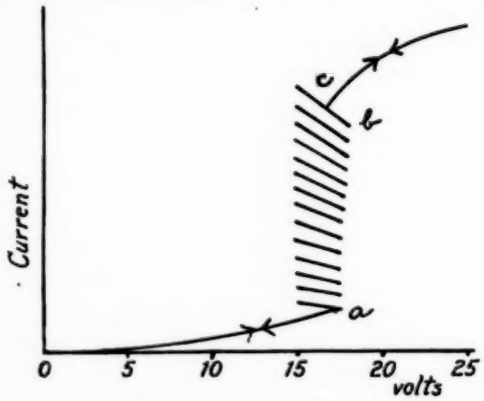

Fig. 6. Oscillations in pure nitrogen; *a* at 17.5, *b* at 18.0, *c* at 16.9 volts.

pendent trials, the point *c* in the figure was located at $16.90 \pm .07$ volts. Further evidence in support of the 16.9 value for the ionization potential of the nitrogen molecule will be given when we take up oscillations in the mixture of the two gases.[20]

When nitrogen was mixed with hydrogen, the breaking potential of the arc was consistently lowered with the increase of nitrogen until the ratio to hydrogen was unity. Further increase in nitrogen raised the breaking potential again until finally it reached the breaking potential in nitrogen alone as the limit. These points are illustrated in Fig. 7. As in the case of mercury vapor and hydrogen, we again assume that the voltmeter recorded only the mean of oscillations. If this view is correct, we would expect that the points of lowest breaking potential would correspond to

[20] *Note on ionizing potentials.* It should be noted that the values here reported do not include a correction for contact difference of potential between electrodes. Probably the most accurate determinations are those by Mackay (Phil. Mag. **46**, 828, 1923) who referred them to the ionizing potential of mercury as a known standard value. His values for H_2 and N_2 are 15.8 and 16.3 respectively. The present values of 16.2 and 16.9 compare well relatively and suggest a correction of about 0.5 volts.

oscillations of greatest amplitude (in the direction of lower voltage), which the oscillograph showed to be the case.

The oscillograph characteristics, Fig. 8, for the mixtures of the two gases, further strengthened the evidence for fixing the ionization potential

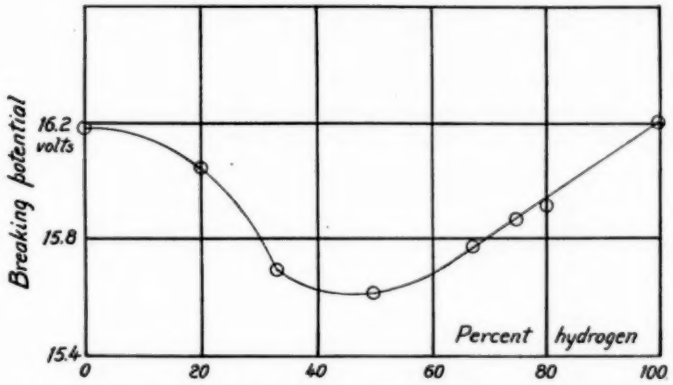

Fig. 7. Breaking potentials in mixtures of H_2 and N_2 in varying proportions.

of nitrogen at about a volt higher than that for the hydrogen molecule. The oscillations of two or three volts amplitude began with the voltmeter reading about 17.0 volts and usually stopped a little below 16.0 volts.

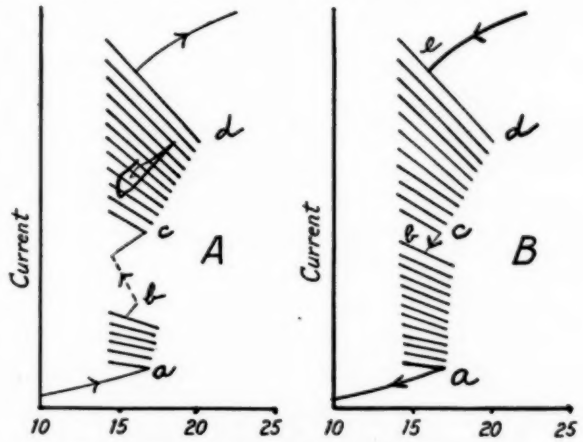

Fig. 8. Oscillations in mixtures of H_2 and N_2.
8A: *a* at 17.0, *b* at 16.0, *c* at 16.9, *d* at 20.2, or 22.8 volts.
8B: *e* at 16.2 volts; other values same as in 8A.

(The decrease in voltage was due to the increase in the arc current of course.) On reaching 16.0 volts, the current increased with a sudden jump and the voltage correspondingly lowered. When the potential was further increased to 16.9 volts, the oscillations started again with a

larger amplitude with its maximum at about 20 or 22.5 volts. Higher filament temperature and excess of hydrogen seemed to favor the higher voltage. When the path was reversed the oscillations came in at 16.2 volts, stopped at 16.9 volts, began again at 16.0 volts, and finally stopped altogether at 17.0 volts, the very point where the oscillations set in in the direction of increasing voltage. This characteristic of reversibility has also been found in mercury[21] and in helium[22] for both of which oscillations have been observed in the low voltage arc.

It seems plausible to account for these phenomena as follows. It is known that the "efficiency" of ionization is much greater in nitrogen than in hydrogen. Thus, at the striking point *a* it is the nitrogen ions which are chiefly responsible for the neutralization of space charge, in spite of the higher ionizing potential of nitrogen. At the breaking point *e*, on the other hand, the electron emission is so great that the necessary amount of ionization can be obtained from the hydrogen. Thus the striking voltage *a* is characteristic of nitrogen and the breaking voltage *e* of hydrogen. It should be noted that the oscillations always set in with increasing current at 16.9 volts (nitrogen) rather than the 16.2 volts (hydrogen) in agreement with the fact that they could be found in pure nitrogen but not in pure hydrogen.

At pressures higher than 1 mm, when there was an excess of hydrogen and when the filament temperature was moderate, there were usually two striking and two breaking potentials, as is shown in Fig. 9. These breaks were accompanied by oscillations and the value of the second striking potential was also determined by means of an oscillograph by observing the maximum peaks in the higher voltage oscillations. The calibration did not give readings more accurately than within half of a volt. The average for 21 trials was 22.7 volts. This agrees unexpectedly well with the result from direct voltmeter reading.

It is not easy to decide just what this potential stands for. Horton and Davis[23] located a critical potential for hydrogen at 22.8 volts, and they attributed it to the ionization of the hydrogen molecule. Brandt[24] and Bazzoni and Waldie[25] observed a critical potential near this value (25.4 volts) in nitrogen. Finally, Smyth observed a critical potential in nitrogen at 24.1 ± 1.0 volts at which doubly charged atomic ions appeared. We shall see that the spectroscopic data suggest that this is

[21] Y. T. Yao, Phys. Rev. **21**, 1 (1923).
[22] Compton, Lilly and Olmstead, Phys. Rev. **16**, 282 (1920).
[23] Horton and Davis, Phil. Mag. **26**, 872 (1923).
[24] Brandt, Zeits. f. Phys. **8**, 32 (1921).
[25] Bazzoni and Waldie, Jour. Frank. Inst. **197**, 57 (1924)

actually a critical potential of nitrogen. Probably the reason for not detecting it in pure nitrogen is that the currents in the latter case were so large that additional effects associated with the second critical potential were masked.

Spectroscopic Observations in Nitrogen and Hydrogen

There are three bands usually associated with the spectrum of ammonia; the ultraviolet band between 3295 and 3432A, the Schuster bands at 5635 and 5682A and the alpha band which extends throughout the greater part of the visible spectrum.

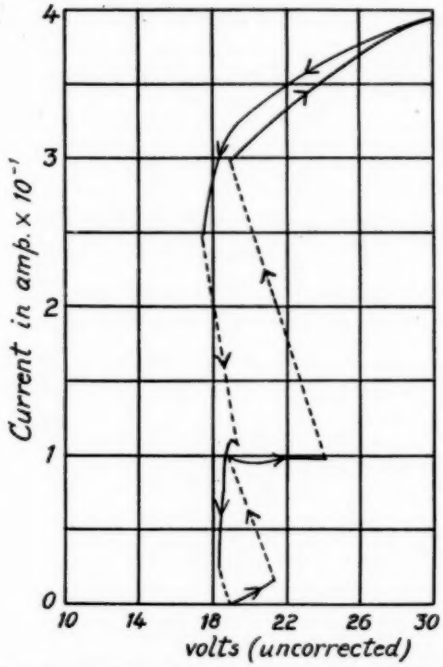

Fig. 9. The two striking potentials in mixtures of H_2 and N_2.

Over ten years ago E. P. Lewis[26] found in vacuum tube experiments that the above mentioned ultraviolet band was present in a mixture of hydrogen and nitrogen with all proportions of the two gases, whereas in each gas alone this band was not found. At the time he attributed it to ammonia. More recently Fowler and Gregory[27] took very precise measurements of the wave-lengths of this band and arranged them into seven series according to their frequency differences. They found by comparison that the ultraviolet band is represented in the solar spectrum.

[26] E. P. Lewis, Astrophys. Jour. **40**, 154 (1914).
[27] Fowler and Gregory, Phil. Trans. **A218**, 351 (1919).

Bair[28] studied the ammonia spectrum by means of transformer discharges and found that the ultraviolet band appeared when the gas was flowing but not when it was at rest. He reported also that the insertion of a small capacity increased the intensity of the band when the gas was at rest and that "mixtures of flowing ammonia and oxygen gave the ultraviolet band with uncondensed discharge." Still more recently W. B. Rimmer[29] measured the more prominent lines of the alpha band and studied the appearance of the various bands under a variety of experimental conditions. He found (1) "no record of the existence of the Schuster bands in the ammonia flame"; (2) "the Schuster bands have given no sign of resolution under high dispersion," and (3) "the effect of a condensed discharge seemed to be to increase the intensity of the ultraviolet band with respect to the Schuster bands."

Rimmer summarized the conclusions reached by the various investigators and his own as follows: "Lewis suggested (corroborated by Barratt and Bair) that the Schuster bands probably represent the true spectrum of ammonia and that the ultraviolet band is probably due to another emission center arising from a more stable combination of N and H other than the normal molecule of ammonia. In addition the present investigation (Rimmer's own work) suggests that the alpha band is due to an emission center which represents a first stage of dissociation of the normal ammonia molecule into more stable forms and the ultraviolet band to an emission center which represents a still more advanced stage of dissociation into constituent atoms."

The writer in studying the spectra in the low voltage arc obtained results similar to those observed by Lewis, namely, that the ultraviolet band was present in the mixtures of the two gases in all proportions but not in each gas alone. The least amount of nitrogen in the presence of hydrogen would cause the appearance of this band. In fact the writer had considerable difficulty in getting rid of this band after the mixture was tried in the tube. When ammonia either wet and dried was used instead of the mixtures, the same band was observable after the arc was struck at about 20 volts.

This ultraviolet band was observable as soon as the arc was struck at about 17 volts, provided there was only one arcing potential observable, and its intensity increased rapidly. It was distinctly observable at between 20 and 25 volts. In such cases, the oscillographs showed that the maximum peaks of oscillations were at about 22 or 23 volts. Under conditions where there were two striking and two breaking potentials,

[28] Bair, Astrophys. Jour. **52**, 301 (1920).
[29] Rimmer, Roy. Soc. Proc. **A103**, 696 (1923).

the ultraviolet band appeared only with the second striking potential, estimated at 22.8 volts, whereas before the second jump, the band was entirely invisible. If the voltage was diminished after passing the second striking potential, faint traces of the band could be seen as low as the first breaking potential at about 15.5 volts. We shall assume that the 22.8 volt potential is responsible for the excitation of the ultraviolet band.

In accordance with the quantum theory of band spectra, the writer has employed Fowler and Gregory's measurements in calculating the moment of inertia of the corresponding molecule based upon the relationship $\Delta\nu = h/4\pi^2 I$, where h is the Planck constant, $\Delta\nu$ the frequency difference, and I the moment of inertia of the molecule. Taking the wave-number difference to be 28.5, I comes out to be $1.95(10)^{-40}$ gm cm^2. This is well within the range of values attributed to the ammonia molecule from measurements of the infrared absorption spectrum of ammonia. Schierkolk[30] found two values: (1) From the band at 10.5μ, I was found to be $1.48(10)^{-40}$ gm cm^2; and (2) from the band at 6.1μ, $I = 2.72(10)^{-40}$ gm cm^2. The difference in these two values Schierkolk attributed to the different orientation of the ammonia molecule. The writer also calculated the moment of inertia from B. J. Spence's[31] measurements of the absorption spectrum at 3μ. Taking the average $\Delta\nu = C \times 19.5$, I would be $2.83(10)^{-40}$ gm cm^2, which is in agreement with Schierkolk's higher value within errors of experiment.

Taking the moment of inertia as $2.8(10)^{-40}$ gm cm^2, if we assume a model for NH in which a nitrogen nucleus and a hydrogen nucleus rotate around their center of mass, the distance between the nuclei is $1.17(10)^{-8}$ cm. If a model for NH_2 were assumed in which the heavy nitrogen nucleus is located at the center of mass and a hydrogen nucleus symmetrically placed on each side, the distance between the hydrogen nuclei would be $1.54(10)^{-8}$ cm. Finally, if we assumed a model for NH_3 to be such that the nitrogen nucleus is situated at the center of a circle in which an equilateral triangle is inscribed at whose vertices the hydrogen nuclei are located, the diameter of such a circle is $1.25(10)^{-8}$ cm. All three values agree reasonably with kinetic theory predictions and therefore, with our present knowledge about molecular arrangements, we cannot decide which of the three types of molecules is responsible for the band. The one conclusion which we *can* draw is that the ***molecule cannot contain more than one atom of nitrogen.*** If two atoms of nitrogen were present in such a molecule, the molecular diameter would have to be of the order of $(10)^{-9}$ cm. We therefore conclude that at 22.8 volts some atomic

[30] Schierkolk, Zeits. f. Phys. **29**, 277 (1924).

[31] Spence, Jour. Opt. Soc. Amer. & R.S.I. **2**, 127 (1925).

nitrogen ions must be present and this is well supported by Smyth's positive ray experiments in which doubly charged atomic ions were found at this potential.

Now to come back to the origin of the 22.8 volt break. In the light of the above discussion we must attribute it to nitrogen and as we shall see later to a production of atomic ions of nitrogen, in all probability. For ionized molecules and atoms (formed by secondary collisions and dissociation due to the filament) of hydrogen were in abundance at the first arcing potential whereas atomic nitrogen ions have never been observed below 22.8 volts. In further support of this view, the negative band of nitrogen at 3914 was observed to come out simultaneously with the ultraviolet band of ammonia and with the appearance of a line. Possibly this is due to a process related to the dissociation of the nitrogen molecule into atomic ions. L. and E. Bloch[32] also observed the appearance of this band at about 22.5 volts.

The so-called Schuster bands, between 5635 and 5822 were entirely absent from the spectrum in the mixtures of the two gases as long as the last trace of water vapor was condensed in the liquid air traps; but when the liquid air flasks were taken away, in three out of four instances, with a different filament each time, the Schuster bands were unmistakably present when the light from a point very near the target was examined. The failure to observe the bands during one of the trials is attributed to the insufficient amount of water vapor present and to the comparatively short distance between the electrodes which made the combination of atoms into more complicated molecules difficult. The writer feels certain that the bands were not due to any material coming out of the target, for in every trial with dry gases, the Schuster and alpha bands were absent when the light from the same part of the arc was focussed on the spectrometer slit.

Thus far our experiment does not tell us whether water vapor or mercury vapor was responsible for the bands. To test this point a few drops of mercury were put in the attached tube and the traps were again immersed in liquid air. We are now sure that mercury vapor alone was present. The Schuster bands were still missing in the spectrum.

Ammonia prepared by evaporation from concentrated solution and stored over potassium hydroxide sticks was next admitted into the system. Well dried gas showed no trace of the Schuster bands. When either water vapor or oxygen in small amount was mixed with it, the Schuster bands invariably came out. The filament at this stage, as would be expected, burnt out very rapidly.

[32] L. and E. Bloch, Comptes Rendus, **175**, 225 (1921).

A further point of interest is the fact that the Schuster bands appeared only when the potential was raised to 70 volts or over, which in Duffendack's experiments was the critical potential for the formation of "active nitrogen."

In the light of these facts, the writer is not able to concur with Rimmer and Bair as to the origin of these bands, namely that the Schuster bands originate from the normal ammonia molecules and the ultraviolet band belongs to a more stable combination of N and H, possibly other than ammonia. The test in dry ammonia with and without a small oxygen content seems conclusive with respect to this point.

Moreover, if these bands were due to ammonia, the high voltage at which these bands appeared would not harmonize with the experiments of Andersen and of Storch and Olson, who found that ammonia was produced at the striking of the arc. The potential difference cannot be accounted for by any theory of secondary collisions.

A study of the conditions under which the Schuster bands have been previously observed unmistakably supports the writer's point of view. Schuster,[33] the discoverer of these bands, observed them for the first time when he introduced "a few drops of a strong solution in water" into the vacuum tube and the discharge was passed while the tube was being evacuated. Lewis and Bair maintained the visible bands only when a continuous stream was allowed to pass through the tube. Under such conditions traces of water vapor were likely to be present. Rimmer's best results were obtained when he evaporated ammonia from a strong solution, employing a water pump for evacuation. In general these experiments did not show that water vapor was not present.

The writer therefore ventures to suggest that the Schuster bands are due to a heavy molecule containing atoms of hydrogen, nitrogen and oxygen, possibly NH_4OH, which is extremely unstable and can be formed only when there are nitrogen atoms in a highly excited state such as are obtainable at 70 volts in the low voltage arc. This type of molecule will explain some of Rimmers observations and account for the unresolved character of the band as due to its large moment of inertia. Then too, we would not expect these bands to be present under conditions of low excitation such as in the oxygen flame.

The above analysis suggest as a consequence that the ultraviolet band originates from the anhydrous ammonia molecule itself. Since there were no other bands observable in dry mixtures of nitrogen and hydrogen up to 120 volts in addition to the hydrogen and nitrogen

[33] Schuster, Report British Association (1872).

spectra, although ammonia is formed, it is reasonable to attribute it to ammonia rather than to NH or NH_2 which up to the present have not been observed as temporary products of such arcs.

Perhaps a question may be raised in reference to Storch and Olson's experiments in which they found that ammonia was formed as soon as the arc was struck whereas in our experiment the ultraviolet band is associated with 22.8 volts. There are two possible answers to such an objection. In the first place it is possible that N_2H_6 molecules may be formed which finally dissociate into NH_3 molecules. Such a process would, of course, be much less probable than the direct formation of ammonia at 22.8 volts and may account for the marked increase in the rate of reaction at 23 volts in all of the curves that were published by Storch and Olson. The coincidence of the first and most distinct jump after the arcing potential in the curves of these authors with our 22.8 volt potential is probably not accidental. In the second place, the discrepancy may be due to a difference in the sensitivity of the two methods of detection.

In conclusion, the writer takes this opportunity to express his sincere thanks and grateful appreciation to Professor K. T. Compton for suggesting this problem and for his constant guidance and inspiration throughout this investigation. He acknowledges also with pleasure his indebtedness to Mr. C. C. Van Voorhis and Dr. L. A. Turner for their help in several matters of technique.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
June 6, 1925.

ON A CLASS OF ONE-VALENCE-ELECTRON EMITTERS OF BAND SPECTRA

By Robert S. Mulliken*

Abstract

Bands emitted by one-valence-electron molecules.—*Series A: BeF, BO, CO^+, CN, N_2^+.* These molecules each contain, like the Na atom, 8+1 electrons outside the nuclei and K electrons. The bands of CO^+ (the comet-tail, negative Deslandres and new quadruple-headed bands reported by Baldet and Johnson) are particularly discussed and analogies to the bands of BO and of CN are pointed out, as well as analogies between the bands of N_2^+ and of CN. The data for BeF bands are less complete. The lines of the known band systems of all these molecules can in each case be expressed as combinations of three electronic terms (each of course with a variety of vibrational and rotational states). These are a singlet term *N* probably belonging to the normal state, a doublet term *A* corresponding to the first excited state, and a singlet term *B* corresponding to the second excited state. There is evidence that the average angular momentum of the emitting electron—which is presumably the odd ninth electron—is the same for the *N* and *B* states, but different for the doublet *A* state; presumably the former resemble *s* states, the latter resemble (inverted doublet) *p* states. In the cases of BO and CO^+, all of the three conceivable combinations between *N*, *A*, and *B* are known; two are known in the case of CN, and one in that of N_2^+; the systems not yet observed probably lie in the infrared. There is a remarkable parallelism between the spectra of the several molecules mentioned in respect to structure of analogous band systems and to molecular constants of corresponding electronic states (cf Table I). *Series B:MgF, AlO, SiN.* These molecules contain an additional electron shell. They are the probable emitters of band spectra which show marked analogies to those of BeF, BO and CN. *Additional series* of emitters are represented by CaCl, SrBr, etc.

Suggested grouping of bands according to the number of valence electrons of the emitters.—Molecules with no unused valence electrons—HF, LiF, BN, NaCl, etc.—show analogy to the rare gases; they do not emit electronic band spectra. Molecules with two excess electrons—CO, NO^+, N_2, SiO—should show analogies to alkaline earth metals. The odd multiplicity of N_2 agrees with this suggestion. Molecules with three excess electrons, e.g., NO, should resemble Al; in fact the bands probably due to NO show even multiplicity.

Nature of multiplicity in band spectra.—Two causes of multiplicity are suggested: (a) connected with the interaction of the emitting electron with the rest of the molecule, and (b) attributed by Kratzer to the interaction of the angular momentum of the emitting and other electrons with that of the nuclei. Examples of each are discussed.

Emitters of certain bands.—*Second negative N_2 bands of Duffendack* may be due to neutral nitrogen molecules in each of which two electrons are initially excited. Evidence is presented for attributing the familiar *aluminum bands* to AlO.

* National Research Fellow.

IN previous papers[1,2] attention has been called to a class of alkali-metal-like diatomic "odd molecules" containing one easily excited electron, and giving rise to conspicuous band spectra. These molecules do not appear in ordinary chemistry, doubtless on account of the activity of this odd electron. Except for the odd electron, these molecules have just enough electrons to form one or more rare gas shells. From the elements of the first and second series of the periodic system the following two series of such molecules are possible:

Series A:	Li	BeF	BO	CN
Series B:	Na	MgF	AlO	SiN

In each case the positive valence of the more electropositive atom exceeds by one the negative valence of the other atom, thus leaving one of the former's valence electrons free as in an alkali metal atom. Numerous additional examples of this type are possible with homologous elements of higher atomic weight; some of these (of which CaCl is typical) have been previously discussed.[2] Such ionized molecules as CO^+ and N_2^+ also belong with series A. The spectra of the compounds of this type, like those of the alkali metals, show the presence of electronic doublets. Series A differs from B or other possible series in that the total number of electrons is sufficient only for one group of eight, so that, as was suggested previously,[1] it may be that the two nuclei share an octet and that, at least when the nuclear charges are nearly equal, the molecule as a whole specifically resembles a Na atom. The electropositive atoms in the molecules of series A and B and similar series might also be considered, at least for the earlier members of each series, as "stripped atoms" whose lost electrons, however, now attached to the electronegative atom, still exert a considerable screening effect.

The chief object of the present paper is to bring together evidence that the molecules of series A and B are indeed all ready emitters of band spectra, and to show from these spectra, so far as is possible with the data available, that these molecules are closely similar to one another in many respects. This will be preceded by a brief discussion of the question of multiplets in band spectra.

Multiplicity in Band Spectra

Mecke[3] has recently discussed the question of multiplets in band spectra and has attempted to set up a formal analogy to the relations

[1] R. S. Mulliken, Phys. Rev. **25**, 259-294 (1925), especially pp. 290-1.
[2] R. S. Mulliken, Phys. Rev. **26**, 1-32 (1925), especially pp. 29-32.
[3] R. Mecke, Zeits. f. Phys. **28**, 261-77 (1924).

which hold in line spectra. He assumes the angular momentum of the emitting electron and of the nuclei, in molecules, to be respectively analogous, in determining multiplet structure, to the angular momentum of core and of emitting electron in atoms. But it seems to the present writer that the real situation must be more complicated, and that there should be two distinct causes of multiplicity in band spectra, (*a*) one connected with the interaction of the emitting electron with the rest of the molecule, as in the case of excited electron and atom-core in line spectra, and (*b*) another which has been attributed by Kratzer[4] to the interaction of the angular momentum of the emitting and other electrons with that of the nuclei. Cause (*a*) gives the most obvious explanation of the occurrence of systems of bands having true multiple origins and two or more widely-spaced heads for each band, separated by a frequency-interval which remains constant or nearly so throughout the spectrum. In the following this will be called multiplicity of class *a*. Examples of this are the doublet α bands of BO ($\Delta\nu = 126$), the interesting doublet alkaline earth halide bands,[2] the doublet β ($\Delta\nu = 87$) and γ ($\Delta\nu =$ about 111) bands of NO, the red CN bands ($\Delta\nu =$ about 54) and, particularly striking because the structure has been analyzed in detail, the doublet bands of CO^+ ($\Delta\nu = 126$). Except in the β bands of NO, each doublet component or sub-band has two heads ($\Delta\nu = 13$ for BO and about 13 for CO^+ and 19 for NOγ), giving an apparent quadruplet structure. But Baldet's work[5] on the comet-tail bands of CO^+ shows that here the two heads belong to a Q and an R branch, respectively, and it is probable (contrary to the assumption made in previous papers[1,2] in the cases of BO and the alkaline earth halides) that the *small* $\Delta\nu$ is not an electronic doublet in any of the above cases. The cuprous halides[2] show possible further examples of class (*a*), differing, however, from the above cases, as might be expected from the much larger $\Delta\nu$ values, in that the molecular constants (vibration frequency, etc.) differ considerably for the various initial electronic states comprising the multiplet.

An apparently distinct type of multiplicity in band spectra, which will here be called *b*, is the "fine structure," according to the nature of which bands have been classed by Heurlinger as singlet, doublet, and triplet bands.[6] Singlet bands may consist of single lines or of doublets whose separation increases steadily with the rotational quantum number, from

[4] A. Kratzer, (a) Ann. der Phys. **71**, 72 (1923); (b) Zeit. f. Phys. **16**, 353 (1923); (c) **23**, 298 (1924); (d) Naturwissenschaften **27**, 581 (1923).

[5] F. Baldet, Compt. Rend. **180**, 820 (1925).

[6] T. Heurlinger, Dissertation, Lund 1918. Cf also review by R. Mecke,[23] who gives an excellent description and diagrams of the various types of fine-structure multiplets.

zero or nearly so at the origin; the violet CN bands are an example of the latter type. Heurlinger doublet and triplet bands have relatively wide separations near the origin, but the components approach each other with increase in the rotational quantum number; each component may in addition show doublet structure of the violet CN type. The structure of Heurlinger singlet and doublet bands has been explained by Kratzer in terms of cause *b*; but there are difficulties,[7] especially in the case of triplet bands,[3] and it may be that class *a* and class *b* multiplicity are not wholly distinct except as limiting cases. Causes *a* and *b* should in general both operate, it would seem, to produce whatever complexity is observed.

Analogy Between the Bands of CO^+, BO, CN and N_2^+

Let us now turn to a detailed consideration of the molecules of series A and B. The so-called comet tail bands and the first negative carbon bands of Deslandres are always obtained together and have been attributed to CO by nearly all who have studied them;[8,9,10,11] in particular, Baldet has obtained them in pure CO.[11] Recently it has been found[12,13] that these two systems of bands have a common final electronic state. They are obtained at very low pressures, or near the cathode at somewhat higher pressures[9]—conditions where ionization is to be expected. Under similar conditions Baldet[11] obtains the N_2^+ (negative nitrogen) bands when a little N_2 is introduced. They are also obtained when traces of carbon compounds are added to helium at 20 mm pressure; perhaps here the excitation occurs in impacts with metastable excited He atoms whose energy (about 20 volts) is approximately that required to simultaneously ionize and excite the CO molecule so as to give rise to the emission of these bands. Under similar conditions,[10] traces of N_2 give the N_2^+ bands. The above facts, together with the extraordinary analogy which these systems of bands present to the α and β bands of BO,[1] make it practically certain that they are due to the CO^+ molecule, which has

[7] R. T. Birge, Phys. Rev. **25**, 240 (1925) (abstract No. 21).

[8] A. Fowler, Month. Not. Roy. Astron. Soc. **70**, 176 (1909); **70**, 484 (1910); Astrophys. J. **35**, 85 (1912); and earlier work of Deslandres.

[9] P. R. Merton, and R. C. Johnson, Proc. Roy. Soc. **103***A*, 383 (1923).

H. B. Lemon, Proc. Nat. Acad. Sci. **11**, 41 (1925). Cf also W. Jevons, Phil. Mag. (6), **47**, 586 (1924), in regard to the Deslandres bands.

[10] R. C. Johnson, Proc. Roy. Soc. **108A**, 343 (1925).

[11] F. Baldet, Compt. Rend. **178**, 1525 (1924); **180**, 271, 1201 (1925).

[12] C. M. Blackburn, Phys. Rev. **25**, 888, 1925 (abstract); other preliminary results, Proc. Nat. Acad. Sci. **11**, 28 (1925); and unpublished work.

[13] R. T. Birge, Nature, **116**, 171 (Aug. 1, 1925)

the same number of electrons as BO, presumably arranged in a very similar manner.

Analogy of CO^+ to BO bands. The quadruple-headed comet-tail bands in the visible are clearly analogous to the α bands of BO; the identical values of $\Delta\nu$ (cf above) in the two cases are particularly striking. Preliminary results of an analysis of these bands have been given by Blackburn[12] and by Baldet[5]; they show that each comet-tail band consists of two closely similar sub-bands which are nearly superposable by a translation of about 126 units along the wave-number axis, thus clearly constituting a class (*a*) doublet. Blackburn's analysis of the CO^+ bands, which he has kindly rendered available to the writer before publication, shows that the lines can all be expressed as the difference of two sets of terms of the form:

Initial: $F_i'(n',m') = \nu_i^e + F'(n') + B_i' {}^n m'^2 + \ldots$ (m' = nearly integral.)

Final: $F''(n'',m'') = F''(n'') + B'' {}^n m''^2 + \ldots\ldots\ldots$ (m'' = half-integral).

Here $F(n) = an - bn^2 + \ldots\ldots$, n being the vibrational quantum number, while m is the nuclear rotational quantum number. For the two sub-bands, ν_i^e differs as already indicated, $F'(n')$ is nearly if not quite identical, while B_i' differs slightly. As shown by Baldet,[5] each sub-band consists of a P, a Q, and an R branch, the latter two giving the two observed heads. Baldet also finds a second intense Q branch (Q′ branch), which is apparently absent under the conditions used by Blackburn. If in the latter case the direct excitation of the CO is by excited He atoms, the situation may parallel that of the β bands of BO as excited in the arc and in active nitrogen.[1] In the arc the β bands show a doublet structure, while in active nitrogen one component of each doublet is missing.

The single-headed ultraviolet first negative Deslandres' bands, as studied by Blackburn, show marked analogy to the β bands of BO. The data on these bands are not such as to permit a wholly independent analysis, but on the very probable assumption that, in view of the identity of $F''(n)$ for the two systems,[10,11] $F''(n'',m'')$ is identical for the two, the analysis shows that $\Delta m = \pm 1$, hence that m', like m'', has half-integral values—all quite as in the violet CN bands. Hence the Deslandres' bands probably consist of normal P and R branches of the violet CN type, except for the apparent absence of the class (*b*) doublets which are characteristic of the latter.

In addition to the two systems of CO^+ bands above discussed, which, like the α and β systems of BO, are both shaded toward the red, some additional quadruple-headed bands which are shaded toward the violet

have been reported by Baldet[11] and by Johnson.[10] They have the same major doublet separation ($\Delta\nu = 126$) as the comet-tail bands, although the minor doublet separation ($\Delta\nu = 25$, according to Johnson) is different. A study of the data shows that they form a system having for their initial electronic state the initial state of the negative Deslandres' bands, and for their *final* electronic state the *initial* state of the comet-tail bands; on this basis the bands observed by Baldet have the vibrational quantum numbers $(n',n'') = (0,1)$, $(0,0)$, and $(1,0)$, while the bands observed by Johnson correspond to $(0,1)$, $(1,2)$, $(0,0)$, $(1,0)$, $(2,0)$, and $(3,0)$—except that the absolute n'' values are subject to the same uncertainty which is present in the n' values for the comet-tail bands (cf note to Table I). The fact that the bands are shaded toward the violet follows at once from the analysis of the other two systems as discussed in the preceding paragraphs, for according to this B is greater (see Table I) for the initial state of the Deslandres' bands than for that of the comet-tail bands, hence $C(=B'-B'')$ is here positive. The different minor doublet separation is also to be expected; the structure of the bands is presumably of the P, Q, R type, like the comet-tail bands, but with the P and Q, instead of the Q and R branches, forming heads. This third system of CO^+ bands is evidently completely analogous to the "combination system" of BO bands,[1] except for the probably superficial difference that only the Q heads are conspicuous in the latter.

Table I summarizes the molecular constants determined by the analysis of the CO^+ bands. Comparative data are also given on BO. From the close analogy to CO^+ it is now probable that the four heads (A_1, A_2, B_1, B_2) of the α bands of BO are R and Q heads (R_A, Q_A, R_B, Q_B, respectively) corresponding to a double electronic level, and not R heads corresponding to a quadruple level, as previously[1] assumed. Considerable independent support is given to this conclusion by the previously somewhat mysterious fact that the combination bands of BO (ref. 1, pp. 284-7) each show only two strong heads instead of four. These strong heads are no doubt the beginnings of Q branches (it may be noted that the Q heads are more intense than the R heads in the α bands); P and R branches may well also be present, the former giving rise to heads, but evidently of low intensity since their presence was not detected except perhaps in one or two cases. The positions of the heads of the combination bands can furthermore be correctly calculated, as should be possible on the above basis, by subtracting observed positions of Q_A and Q_B α heads from calculated positions of suitable β band-origins. In spite of the changed interpretation of the bands, no change is required in the values of B' and B'' previously given, nor in the interpretation of the β

bands, nor in other essential results (such as the existence of half-integral vibrational quantum numbers) of the discussion previously given.

Analogy to CN bands. It is probable that there is a more or less complete analogy between the comet tail and Deslandres' bands of CO^+, the a and β bands of BO, and the red and violet CN bands. The doublet structure and quadruple heads of the comet tail bands and the a bands of BO again appear in the red CN bands; in all three cases the doublet component of longer wave-length is the more intense, as if due to an *inverted* pair of p-terms for the initial state. In each case the larger doublet separation is more or less variable; in BO, slight variability was reported by Jevons, although not noted by the present writer[1]; in CO^+, Baldet reports a change from $\Delta\nu$ = about 17 at $\nu = 18{,}000$ to about 10 near $\nu = 31{,}000$; in CN (for data cf Kayser-Konen, Handbuch der Spektroscopie, Vol. VII), the smaller $\Delta\nu$ changes for the low-frequency pair of heads in each band from about 18 near 14700 to 15 near 21000, and from about 28 to about 21 in the same range for the high-frequency pair, the head of highest frequency also being unusually weak (probably because it corresponds to a relatively high rotational quantum number). This evidence points strongly to a close resemblance in structure for the a BO and the red CN bands to the P, Q, R comet-tail type, with its true doublets (large, constant $\Delta\nu$), and its false doublets (small, variable $\Delta\nu$) corresponding to the separation between a Q and an R head; the marked inequality of the two small $\Delta\nu$'s in CN may be attributed to an unusually large difference in the values of B' for the two components of the true doublet, combined with a relatively small value of $C(C = B' - B'')$.

Discussion of electronic states of the molecules. The above analogies are present to a marked degree in the $F(n')$ and $F''(n'')$ coefficients and in the values of ν^e, as is shown in Table I, which summarizes the available data from the band spectra of the molecules of series A and B. These coefficients, it may also be noted, vary in a more or less systematic manner with the atomic number or weight. The values of the vibration frequency (a') and of the moment of inertia (equal to $h/8\pi^2B'$) suggest in each case a markedly lesser stability of the molecule for the *first* than for the *second excited state* of the molecule in spite of the smaller energy of electronic excitation in the former. Apparently the motion of the excited electron is of a quite different type for the two excited states, and furthermore differs less in the second than in the first excited state from that in the common final, probably normal, state. This is understandable in terms of Kratzer's interpretation[4] of bands for which $\Delta m \neq \pm 1$ or 0. Such bands are explained by postulating that the resultant electronic angular momentum changes in such a way that $\Delta j = \pm 1$ or 0,

where j is the quantum number corresponding to the *total* angular momentum (analogous to the inner quantum number in line spectra), and here equal to the vector sum of the electronic and nuclear rotational quantum numbers ρ and m. In case the latter two are parallel, $\Delta j = \Delta m + \Delta\rho = \pm 1$ or 0. In the comet tail bands, where Δm is not equal to 0 or ± 1 (and presumably by analogy in the red CN and α BO bands) $\Delta\rho$ must certainly differ from zero if $\Delta j = \pm 1$, 0, whereas in the Deslandres and violet CN bands—and presumably in the β BO bands—with $\Delta m = \pm 1$, the simplest assumption is $\Delta\rho = 0$. The simplest explanation of the latter ($\Delta\rho = 0$) is that the average angular momentum of the *emitting electron* —which in the case of odd molecules of the CN type is presumably the "odd" electron and presumably is the *only* electron whose quantum numbers here change—does *not* change during emission (cf Kratzer,[4a] p. 83) but that in the former ($\Delta\rho \neq 0$) its angular momentum *does* change in direction if not in magnitude. The relations mentioned above between the characteristics of the molecule in its different electronic states may then be correlated with the average angular momentum (and perhaps with an azimuthal quantum number) of the emitting electron. Furthermore, the presence of class a doublets for the *first excited* state in these molecules, and their absence in the *normal* and in the *second excited* state, are now explained if the two latter, which have *the same* ρ, are of the nature of s states, while the former, which has a *different* ρ, is of the nature of an inverted doublet p-state. (This is of course contrary to a suggestion made in a previous paper[1] as to a possible analogy of the two excited states to the $2p$ and $3p$ states of the Na atom.)

Analogy between bands of N_2^+ and CN. The very close resemblance of the CO^+ spectrum to that of BO is probably parallelled by a similar analogy between the spectra of N_2^+ and CN. The "negative nitrogen" bands, which are definitely known to be due to N_2^+, resemble the violet CN bands extremely closely in structure (including the appearance of the CN type doublets)[14], in position in the spectrum, and in the relative values of the coefficients of n' and n''. Although no second system of N_2^+ bands has been found analogous to the red CN bands, it may well be that these lie in the near infrared so as to have escaped observation. The fact that the negative nitrogen bands have been obtained by Duffendack[15] in the low-voltage arc at a potential just about enough above the ionizing potential to correspond to ν^e (3.2 volts), indicates that their final

[14] M. Fassbender, Zeits. f. Phys. **30**, 73 (1924).
[15] O. S. Duffendack, Phys. Rev. **20**, 665 (1922); Astrophys. J. **61**, 221 (1925).
[16] R S. Mulliken, Cf Nature, Dec. 13, 1924.
[17] O. S. Duffendack, and D. C. Duncan, Phys. Rev. **23**, 295 (1924).

state must be the normal state of the N_2^+ molecule, again in analogy to the CN bands[16] and the BO bands.[1]

Simultaneously with the negative nitrogen bands, according to Duffendack and Duncan,[17] a new system appears further in the ultraviolet; these Duffendack[15] has called the *second negative bands*. Since ν^e here considerably exceeds the value which it has for the first negative bands, according to Duffendack,[15] it seems probable, however, that these bands are not emitted by the N_2^+ molecule but by a neutral molecule in which both of the final pair of electrons (whose analogy to the pair of valence electrons of such a metal as Mg has been suggested above) are excited.

The negative nitrogen bands differ from the other bands of their class in showing a peculiar alternating intensity in each branch which has led Dieke[18] to propose a subdivision of each branch into two. This peculiarity, however, seems to be characteristic of homopolar molecules,[19] and the proposed change, as first pointed out by Birge (private communication), would involve a conflict in the calculated moment of inertia and internuclear distance (cf Table I) with the remarkably consistent and reasonable values obtained by the usual interpretation for all the members of this class of emitters (and for related molecules such as N_2 and CO). Dieke's interpretation would halve the value of r_0 given in the table for N_2^+.

Other One-Valence-Electron Bands

Of the members of series A and B above, BO and CN, and their analogues CO^+ and N_2^+, have now been discussed; BeF and MgF are the probable emitters of the known[20] beryllium and magnesium fluoride bands (cf Table I and notes); there remain SiN and AlO. The SiN bands, first described by Jevons[21] and recently studied by the writer,[22] show close analogy to the violet CN bands.[22] From this one might expect in the red or near infrared a system of SiN bands analogous to the red CN bands. Although no such bands have been detected, a new double-headed system ($\Delta\nu = 27$) has been found[22] whose final state may possibly be the same as the initial state of the hypothetical red SiN bands.

Bands of AlO. The last member of series A and B is accounted for if the familiar *aluminum bands* centering in the green are attributed to AlO.

[18] G. H. Dieke, Zeits. f. Phys. **31,** 326 (1925).

[19] R. Mecke, Zeits. f. Phys. **31,** 709 (1925). This characteristic of homopolar molecules was also independently pointed out (private communication) by R. T. Birge.

[20] S. Datta, Proc. Roy. Soc. **99A,** 436 (1921 ; **101A,** 187 (1922).

[21] W. Jevons, Proc. Roy. Soc. **89A,** 187 (1913).

[22] R. S. Mulliken, Nature, (March 22, 1924) and (July 4, 1925); Phys. Rev. **26,** 319 (September 1925).

The question has long been in dispute[23] as to whether these bands are due to the metal or to the oxide. Since the structure of the bands is that of a diatomic emitter, the alternatives are Al_2 and AlO. The isotope effect is unfortunately not available as a criterion, on account of the absence of Al isotopes. The vibration frequencies in the initial and final states[24] (cf Table I) for the bands in question are of the same order of magnitude as for SiN, and are more in accord with the undoubtedly tightly-bound AlO than with a loosely-bound compound such as Al_2 whose bands would presumably resemble the Na_2 bands. Also Mörikofer has shown that the bands are emitted in all parts of the Al arc, indicating that, although easily excited, their emitter is also stable under more violent conditions.[25] Furthermore, the results of an unpublished calculation from measurements on structure lines, made by W. C. Pomeroy and R. T. Birge and kindly rendered available to the writer, give for AlO an internuclear distance 1.615×10^{-8} cm, not far from that of SiN. The corresponding calculated value 1.38×10^{-8} for Al_2 seems too small for a loosely-bound molecule composed of two atoms with complete shells and with three additional outer electrons in fairly large orbits. The larger values of r_0 for AlO and SiN than for BO and CN are in accord with expectation, on account of the extra electron shell present in the positive ions of the former. Also, the structure of the bands is of the violet CN doublet type.

The great affinity of aluminum for oxygen, and the analogy to BO, also favor AlO. Experiments by the writer show that the bands are obtained in active nitrogen under the same conditions as are required for the BO bands. $AlCl_3$ vapor was introduced into active nitrogen containing varying amounts of oxygen. With no oxygen, a weak continuous spectrum in the visible resulted. When enough oxygen was added so that the β bands of active nitrogen (NO bands) exceeded in intensity the α bands (N_2 bands), the bands which are here attributed to AlO became faintly visible; the strongest heads were identified both visually and photographically.[26]

Analogies in Other Series of Bands

Two-valence-electron bands. If the molecules of series A and B resemble alkali metal atoms, molecules having one more electron, such as CO, NO^+, N_2, and SiO, should show analogies to the alkaline earth metals,

[23] H. Kayser and H. Konen, Handbuch der Spektroscopie, Vol. 7, section on Al.

[24] R. Mecke (Phys. Zeit. **26**, 235, 1925) gives the equation for the heads.

[25] R. Mörikofer, Dissertation, Basel, 1925.

[26] It cannot be stated positively that the bands were not weakly present (and obscured by continuous background) when the nitrogen was free from oxygen; but there is no evidence for this.

e.g., in degree of multiplicity of electron levels and (cf above under N_2^+ in regard to simultaneous excitation of electrons in N_2) in occurrence of double electron jumps. The change from odd to even multiplicity shown

TABLE I

Constants of emitters of the CN type

Emitter	ν^0	Excited states a'	b'	B_0'	$r_0(10)^2$	Probable normal state a''	b''	B_0''	$r_0(10)^2$
BeF	33180-33215	1157	8	....	....	1250	12	....	....
	Below λ2200?	....	....	....	....				
$B^{11}O$	23522-23648	1248	10.6	1.92	1.20	1873	11.8	2.30	1.09
	42881	1269	10.0	2.03	1.16				
CO^+	20346-20472?	1550?	14.1?	1.56	1.28	2199	15.5	1.97	1.14
				1.60	1.26				
	45637	1701	26	1.80	1.19				
CN	14376-14430	1728	13.5	<1.89>	1.17	2056	13.5	1.89	1.17
	25800	2244	20.3	1.96	1.13				
N_2^+	Near infra-red?	....	....	....	....	2187	16.1	1.92	1.12
	25547	2398	26.2	2.07	1.08				
SiN	Near infra-red?	....	....	....	....	1145	6.6	0.74	1.55
	24234	1016	17.8	0.73	1.56				
AlO	Near infra-red?	....	....	....	....	971	7.2	0.64	1.62
	20646	866	4.0	0.61	1.65				

Notes for Table I. General: the values of ν^0, a, and b are for *heads*, except in the cases of SiN, the violet CN bands, and the high-frequency CO^+ bands, and serve merely to give an approximate idea of the true values, except that in the doublet bands, the heads given are Q heads and should nearly coincide with the true ν^0 values; also, the values given would be somewhat changed if half-integral vibrational quantum numbers were adopted, as they probably should be.[1,2]—The constants for BeF are from an analysis of Datta's results (ref. 20); Datta reported only three heads for each band (at 33218, 33215, and 33180 for the 0,0 band), but it is possible that a weak fourth head (the third head is weak) may have escaped notice among the numerous structure lines; although some data are given on structure lines, and the region of the null-line can apparently be located approximately, reliable values of B' and B'' could not be obtained. The formulation of the heads requires a relatively large term in $n'n''$ (about $-5\,n'n''$), which must be due to variation with n' and n'' of the (evidently rather large) distance from head to origin;[27] the fact that the mutual separation of the three observed heads is not constant may be ascribed to this fact combined with the existence of appreciable differences in the values of B for the different heads.—For the low-frequency CO^+ bands (comet tail bands) the constants ν^0, a, and b are as given by Birge,[13] although the true values may be considerably different, due to uncertainty as to the correct assignment of vibrational quantum numbers; the values of ν^0, a, and b for the other CO^+ bands are from Blackburn's published equations;[12] the B_0' and B_0'' values are preliminary values from unpublished work of Blackburn, and involving a revision of his published values. For CN, N_2^+, SiN, AlO, respectively, see refs. 24, 14, etc.; 15; 22; 24 and text.

[27] R. S. Mulliken, Phys. Rev. **25**, 119-38 (1925).

in passing from the spectrum of N_2 to that of N_2^+ (this change being analogous to that expressed by the alternation law in line spectra) has been discussed by Mecke, who has also discussed the application of the displacement law of line spectra to the emitters of band spectra, in particular to hydrides.[3]

Three-valence-electron bands. Further, odd molecules like NO, with one more electron than for the N_2 type, should resemble atoms of the aluminum family; the probable spectra of NO (β and γ bands of active nitrogen, the latter being the same as the third positive nitrogen bands)[1] show electronic doublets (see above), in accord with the expected even multiplicity. Nitric oxide, it may be recalled, is one of the very few substances composed of odd molecules whose chemical activity is sufficiently low to permit its existence in quantity under ordinary conditions.

No-valence-electron bands. Again, going backward from series A and B, molecules of the type of LiF (and HF, NaCl, etc.), BeO, BN, containing no unused valence electrons, should have an analogy with the rare gases; this is indeed borne out by the complete absence[2] of electronic band spectra in the case of the halides (and apparently for BN), but is seemingly contradicted in the case of the alkaline earth oxides by the occurrence of characteristic band spectra (but see discussion in a previous paper[2]).

Note added in proof. Since the above was written, a part of the relations noted have been pointed out independently by R. T. Birge (Nature, August 8, discussion of the combination bands of CO^+) and R. Mecke (Naturwissenschaften, August 7, combination bands of CO^+ and analogies between BO and CO^+; CN and N_2^+).

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
July 3, 1925.

INDIRECTLY EXCITED FLUORESCENCE SPECTRA

By S. Loria*

Abstract

Fluorescence spectrum of thallium mixed with Hg vapor.—(1) *Repetition of experiments of Franck and Cario.* The illuminated end of the quartz tube containing Tl metal was placed in the hottest part of the furnace to avoid condensation. In the fluorescence spectrum all Tl lines to be expected theoretically, from $2p_1-2s$ to $2p_1-4d_1$ and $2p_1-5d_2$ were identified. This excitation shows that the life of the $2p_1$ state is for Tl atoms of the order of 10^{-6} sec. (2) *Enhancing effect of inert gases.* Series of spectrograms with the same tube confirmed the results of Donat. As the pressure of A or N_2 was increased the intensity of λλ5350, 3776 and 2768 increased rapidly reaching a maximum for 5 to 20 mm of A or 5 to 10 mm of N_2. A trace of O_2 neutralizes this enhancing effect. (3) *Experiment with Tl vapor distilling past the window.* In this case a "negative effect" was observed, the addition of a neutral gas decreasing the fluorescence. This was probably due to the interference of the inert gas on the rate of distillation and hence on the amount of Tl present near the window. (4) *Experiments with closed tubes at uniform temperature.* The enhancing effect was also obtained with these tubes, showing that it cannot be an indirect effect of the interference of the neutral gases with the distillation of the Tl vapor in Donat's experiments, but is definitely associated with the presence of the neutral gas. (More intense fluorescence was obtained with N_2 at 5 mm and Hg at 0.16 mm than with N_2 at 8 mm and Hg at 0.5 mm, the Tl being at 0.45 mm.) (5) *Conclusions regarding role of Hg atoms in the $2p_2$ state.* These results confirm the assumption of Franck and Donat as to the part the Hg atoms in the metastable $2p_2$ state take in the energy transfer to normal Tl atoms. Comparison of spectrograms at different partial pressures indicates that the metastable Hg atom may survive many collisions with normal A or N_2 molecules but easily gives up its energy when colliding with normal Tl or Hg atoms, probably more easily to Tl than to Hg.

Introduction

1. Klein and Rosseland[1] concluded from theoretical considerations, based on the application of the second law of thermodynamics to a system of atoms, electrons, and radiation, that so-called collisions of the second kind must occur between activated atoms and electrons. Due to such a collision an activated atom may return to its normal state without sending out the radiation that is connected normally with this transition, the corresponding quantum $h\nu$ being then distributed between both colliding particles in the form of kinetic energy, according to the principle of momentum.

* Professor of Physics at the University, Lwow, Poland.

[1] O. Klein and S. Rosseland, Zeits. f. Phys. **4**, 46 (1921).

2. J. Franck[2] extended this idea of collision of the second kind to a system which contained besides electrons, activated atoms, and radiation, also normal atoms of a suitably chosen vapor. He then predicted that activated mercury atoms, when colliding with neutral atoms of a vapor which does not absorb the effective radiation and which has its resonance potential below 4.9 volts, may excite the atoms of the vapor, causing them to emit their fluorescence spectra. These spectra ought to contain all lines corresponding to transitions from energy levels E_2 to E_1, where $E_2-E_1 \leqq 4.9$ volts. Experimental investigations carried out by Cario,[3] Franck and Cario,[4] Kopfermann,[5] and Donat,[6] confirmed this theoretical prediction in the case of Tl, Cd, Pb, Bi, Ag, and In. On account of the analogy of this excitation of spectral lines with the process of sensitization of photographic plates, Franck called the new phenomenon the "sensitized fluorescence."

3. A closer investigation of the spectra revealed two new facts. (1) Some lines corresponding to energy transfers $E_2-E_1>4.9$ volts appeared on the plates. (2) Abnormally high intensities of some of the lines could not be accounted for by considerations of the theoretical probability of collisions with the required amount of relative energy. To account for these Franck found it necessary to assume (a) that the excitation energy of an activated Hg atom may be added to the relative kinetic energy of the colliding particles, so that the sum of both exceeds under favorable conditions the equivalent of 4.9 volts; (b) that due to collisions some of the activated Hg atoms ($2p_2$ state) may be thrown over into the lower metastable state for a time longer than the life-time in the $2p_2$ state.

4. The correctness of the last assumption seemed strikingly confirmed by some new results obtained by Donat. He found that when A or N_2 is added to the mixture of Hg and Tl showing the sensitized fluorescence of the latter, the intensity of all Tl lines increased remarkably, while the resonance of Hg became weaker. It has been shown that even at atmospheric pressure of A — when, as we know from investigations of Wood,[7] Cario,[3] and Stuart[8] the resonance of Hg vapor is largely reduced— the Tl lines λλ5350, 3776, 3529 and others appear stronger than without A present. This relatively high intensity of the Tl lines in the presence

[2] J. Franck, Zeits. f. Phys. **9**, 259 (1922).
[3] G. Cario, Zeits. f. Phys. **10**, 185 (1922).
[4] G. Cario and J. Franck, Zeits. f. Phys. **17**, 202 (1923).
[5] H. Kopfermann, Zeits. f. Phys. **21**, 316 (1924).
[6] K. Donat, Zeits. f. Phys. **29**, 345 (1925).
[7] R. W. Wood, Phys. Zeits. **13**, 353 (1912).
[8] H. Stuart, Zeits. f. Phys. **32**, 262 (1925).

of a large number of A atoms, when the probability of a collision of an activated Hg atom with an A atom is enormously greater than the probability of its collision with a Tl atom, makes it necessary to assume that many Hg atoms may be thrown over into a metastable orbit $2p_3$ and retain their energy for a relatively long time. This explanation involves, however, a new important assumption as to the nature of the metastable $2p_3$ state of the Hg atoms.

Till now we have defined the metastable state of an atom, according to the requirements of the selection principle, as a state from which the atom cannot come back to the normal state in the ordinary way, i.e., by sending out its surplus energy in the form of radiation. We should expect such an atom to persist in the metastable state indefinitely, provided no collision with another atom and no action of external electric or magnetic fields intervene. Thus, collisions being the only possible mechanism of bringing an atom out of a metastable state, we should expect its time of existence in such a state to be completely determined by its collisions with other atoms. Hence, if we accept Franck's explanation of the increasing effect of A on the sensitized fluorescence of Tl vapor, we have to assume furthermore that the *Hg atoms in $2p_3$ state may endure very many collisions with A atoms or N_2 molecules without going over to a lower state until they happen to collide with a Tl atom*, to which they then transfer immediately the whole amount of potential energy.

It appeared desirable, on account of the peculiarity of this last assumption, to re-examine the phenomena discovered by Franck, Cario, and Donat, repeating their experiments under better defined conditions of temperature and pressure with the purpose of finding, if possible, some other explanation.

I. Indirect Excitation of Thallium Fluorescence in Mixture with Mercury Vapor

5. The experimental method used for excitation of the Tl fluorescence through collisions with activated Hg atoms was quite similar to that used by Franck and Cario.

A Cooper-Hewitt vertical mercury arc, mounted between the poles of a small electromagnet and cooled down by a strong blast of air, was used as source of illumination. A quartz lens (4 cm diameter, 7.5 cm focus) concentrated the unresolved beam of light on a flat window of a quartz tube, illuminating it from the side at about 45°. The tube was in a horizontal position, its shape and dimensions being as shown in Fig. 1 (tube *A*).[9] Within it was placed, in the position indicated by the black

[9] At first 2 mm thick plane polished quartz plates were fused on the end of the tube. It has been found, however, that such windows when heated above 300°C, are very

spot, a piece of carefully purified metallic Tl, the whole being then inserted in an electrically heated furnace with two fused quartz windows as shown. The furnace was built in such a way that the illuminated part of the tube could be kept at a temperature a little higher than the rest, in order to prevent the flat end of the tube from being covered with a thin layer of condensed metal..

The rear end of the quartz tube was connected with a diffusion pump and contained a few cc of pure mercury in a vertical side tube which was heated by another furnace. Provisions were made to keep the part of the tube between the two furnaces at a temperature higher than that of the mercury.

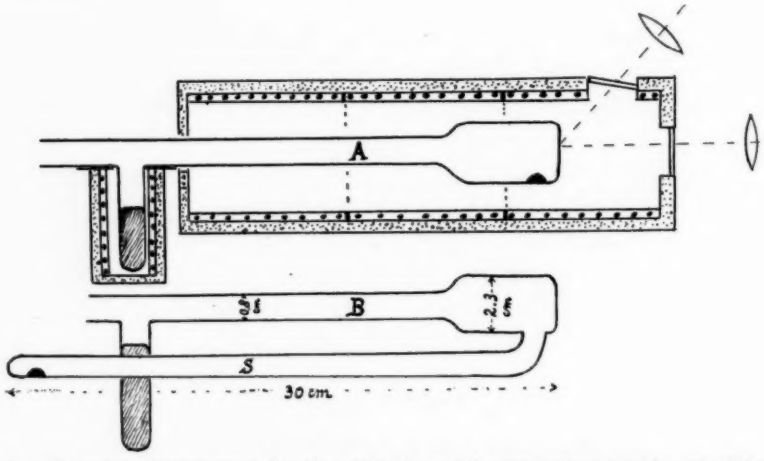

Fig. 1. Diagram of apparatus showing tube *A* used for repeating experiment of Franck and Cario and of Donat, also tube *B* in which the liquid Tl is 30 cm from the window.

A second quartz lens enabled the image of the illuminated window to be thrown upon the slit of a large Hilger spectrograph. Cramer's isochromatic plates (very sensitive in the region of the green Tl lines) gave the most satisfactory results.

6. The first trace of λ5350 could be detected visually in the spectrum when the temperature of the main furnace was about 500°C and the temperature of Hg higher than 60°C. Photographs obtained after one hour exposure with Tl at 800°C and Hg at 100°C show almost all the

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easily attacked by the vapors. They may be cleaned in an oxygen-hydrogen flame, but even then they do not last long and must be too often renewed. Far more satisfactory results could be obtained by simply blowing one end of a sealed-off tube flat. Windows of that kind can be made sufficiently even and plane, and endure many hours of exposure without showing any loss of transparency.

lines that could be expected according to Bohr's energy level scheme. The following lines were identified.

5350	$2p_1-2s$	2918	$2p_1-4d_1$
3776	$2p_2-2s$	2826	$2p_1-4s$
3529	$2p_1-3d_2$	2768	$2p_2-3d_2$
3519	$2p_1-3d_1$	2711	$2p_1-5d_2$
3230	$2p_1-3s$	2580	$2p_2-3s$
2922	$2p_1-4d_2$	2380	$2p_2-4d_2$

The existence of the lines 2711 ($2p_1-5d_2$), 2918 ($2p_1-4d_1$), 2922 ($2p_1-4d_2$) is very significant. It shows that in some Tl atoms electrons have been raised up to $4d_1$, $4d_2$, $5d_2$ levels. Energy equivalent to 4.9 volts is not sufficient to bring them to these levels from the normal $2p_2$ orbit. The energy transfer from Hg atoms must have occurred while the electrons were in $2p_1$ state, brought there by collisions with normal atoms, or more likely on their way back from higher states. The possibility of excitation of lines corresponding to such high energy levels like $4d_1$, $4d_2$, and $5d_2$ shows at any rate that the lifetime of the $2p_1$ state is for Tl atoms at least of the same order of magnitude as the time between collisions of Tl and Hg under our conditions, i.e., about 10^{-6} sec.[10]

II. The Effect of A and N_2 on the Indirect Excitation of Tl-Fluorescence

7. The experimental arrangement remained the same as before, only provisions were made for introducing gases under known pressure.

Argon supplied by the General Electric Company was guaranteed to be 99.8 percent pure, the main impurity being nitrogen. Nitrogen made from air by the ordinary process (ammonium chloride, ammonium hydroxide, and copper) had been passed through a liquid air trap and a tube with hot copper gauze.

The effect of A under different pressures up to 1 atm. is clearly shown in Fig. 2. The first spectrum shows the Franck-Cario effect in Tl without argon. All six following spectra show the Tl lines enhanced by A at

[10] This time may be computed from the well-known equation (L. Boltzmann, Vorlesungen über Gastheorie) for the number of collisions

$$\nu=\sigma^2\, p\times 2666\cdot 6\sqrt{(2\pi N/k\vartheta)\,(m+m_1)/mm_1}$$

where σ = the mean value of the diameters of Tl and Hg; p = the total pressure; $N=0.607\times10^{21}$; k = Boltzmann's constant 1.37×10^{-16}; θ = the temperature, 1073°K; m = the atomic weight of mercury, 200.6; m_1 = the atomic weight of thallium, 204. If we take the diameter of Hg in the normal state, i.e., $3.5.10^{-8}$ cm and the diameter of Tl obtained from the x-ray analysis of crystals, $3.4.10^{-8}$ cm we get $T=1/\nu=2\times10^{-6}$ sec. Assuming that all mercury atoms are activated and have then according to Stuart (H. Stuart, Zeits. f. Phys. **32**, 267, 1925) the diameter $3.4(3.5\times10^{-8}$ cm), we get $T=1/\nu=5.5\times10^{-6}$ sec.

different pressures. This remarkable enhancement of all Tl lines is in agreement with Donat's statement. However, the effect he obtained was different for different lines; some of them showing more or less pronounced maxima at pressures between 1 and 100 mm Hg, whereas no maxima were noticed by him for the lines 5350, 3776, 2768; he reports that their intensities increased rapidly with the pressure to a few centimeters and

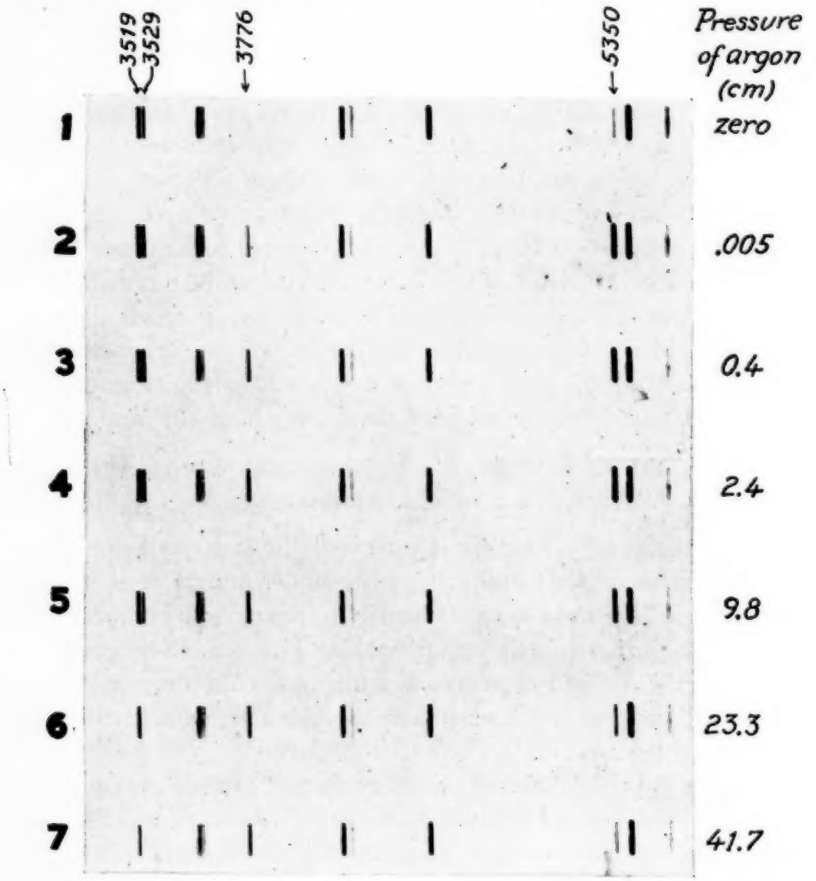

Fig. 2. Spectrograms of fluorescence in mixtures of Tl and Hg vapors, with an inert gas argon also present at various pressures as indicated. The time of exposure in each case was 32 min; the Tl was at 680°C, the Hg at 100°C.

then remained constant up to atmospheric pressure. The results of the present investigation show that a maximum in the effect of A on the intensity of the Tl spectrum appears *on all the lines without exception, but at different pressures.* As may be seen in Fig. 2, the lines 5350, 3776, and 2768 decrease in intensity when the pressure exceeds 2 cm, the optimum being for 5350 between 5 and 20 mm.

The decrease of intensity is naturally explained by the fact that at higher pressures collisions of the second kind must occur as well between argon and excited Tl atoms as between argon and mercury atoms. The maximum is very flat and may not show up as distinctly on photographs taken with longer exposures. This might account for the apparent equal intensity of blackening on Donat's plates.

Fig. 3. Fluorescence spectra of Tl and Hg with N_2 present. Exposure 32 min. Tl at 640°C, Hg at 100°C.

8. Donat found that pure nitrogen influences the Tl spectrum in the same way as A, the effect being, however, much weaker. A careful investigation of this effect at *very low pressures* shows, however, that the effect of N_2 may be even much stronger than that of A, provided the optimum pressure of the gas is used. *It is enough to introduce into the tube a small fraction of a millimeter of carefully purified* N_2 (*about* 2×10^{-3} *mm*) *to* make the whole window shine with vivid, very bright soft green light. The phenomenon is especially interesting when observed through a

spectroscope. The line 5350 flashes out suddenly and, although it had been much weaker than 5461 of Hg, becomes now many times stronger. The sharp maximum may be clearly seen in Fig. 3. Visual observations have shown that the optimum pressure of N_2 is between 5 and 10 mm. It has been noticed also that when nitrogen at this pressure is brought into the tube the intensity of 5461 of Hg increases remarkably. This

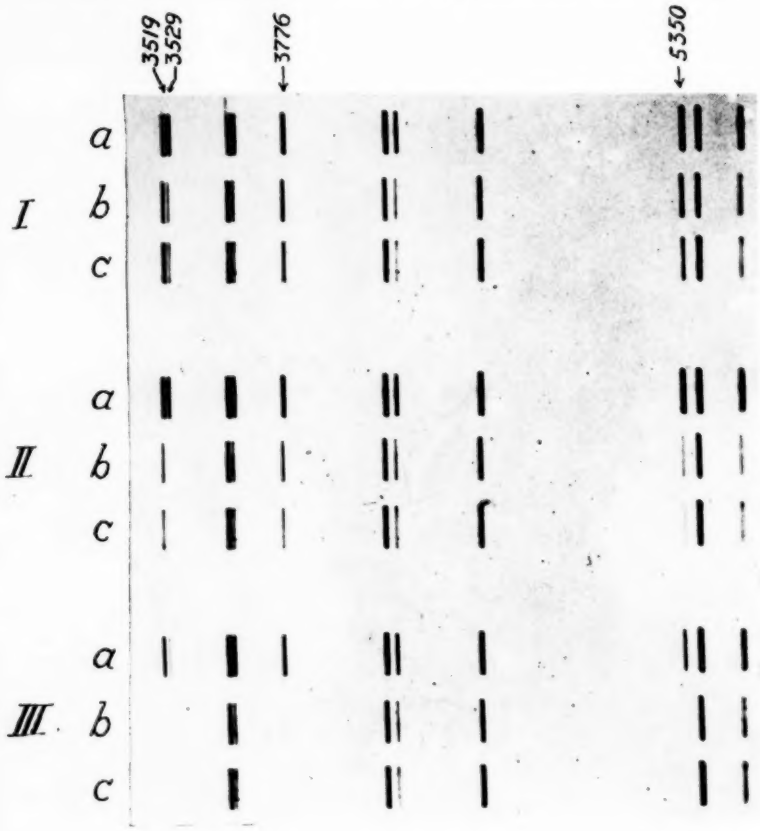

Fig. 4. Fluorescence spectra of sealed off tubes *a*, *b* and *c*.
The temperature was 680°C for group I, 590°C for group II and 490°C for group III.
Tube *a*: Tl saturated; Hg at pressure <0.16 mm; N_2 at 5 mm.
Tube *b*: Tl saturated; Hg at 0.5 mm; N_2 at 8 mm.
Tube *c*: Tl saturated; Hg at 0.5 mm; no inert gas.

observation is in close agreement with the results obtained by Wood in his investigation of the changes in the intensity distribution of the Hg spectrum due to the presence of nitrogen.[11] The effects of N_2 and A

[11] R. W. Wood, Proc. Roy. Soc. **106**, 689 (1924).

on the Tl fluorescence seem to be very sensitive to small traces of impurities, *the most destructive being oxygen.*[12] Nitrogen made from air in the way described above, but not passed over hot copper, extinguished the green Tl line entirely. Also, argon containing a minute amount of air as impurity, weakened the Tl fluorescence remarkably.

9. So far the results of the present investigation are in general agreement with what has been found by Donat.

However, the explanation suggested by him as to the accumulation of energy in the metastable $2p_3$ state of mercury atoms is, nevertheless, open to serious objections. The conditions under which the new phenomenon has been observed, are not at all defined. One part of the tube A, Fig. 1, containing Tl is kept at 800°C, the other with mercury being at 100°C. The saturation pressure of Tl at 800°C is about 2 mm;[13] the saturation pressure of Hg is 0.3 mm.[13] The fluorescence is a surface phenomenon, the whole process of excitation taking place on the illuminated window.

As long as no gas is present in the tube, the thallium vapor diffuses rapidly away towards the colder part of the tube. Its pressure changes from 2 down to 0.02 mm. Moreover, due to the steep gradient of temperature (from 800°C to 100°C in a distance of 30 cm) the stream of Tl vapor condenses on the way and may pump out mercury from the front part of the tube, decreasing its density below 0.3 mm. These processes evidently tend to decrease the intensity of the fluorescence.

These conditions are totally changed when gas is introduced into the tube. The gas brings in fresh mercury vapor, it slows down the diffusion of Tl vapor and it prevents the mercury from being pumped out by the condensing Tl. These changes tend to increase the intensity of Tl fluorescence. It seems, therefore, not improbable that the effect observed might be partially or even totally explained in the foregoing simple way.

Very instructive in this respect were the results obtained in experiments made with the tube B shown on Fig. 1. Metallic Tl placed at a distance of 30 cm from the window was heated by a special furnace and allowed to diffuse along the whole tube, the stream of vapor being carried through the illuminated portion. The green line of Tl λ5350 appeared at about 700°C. Nitrogen of 5 mm pressure *extinguished* the fluorescence instantaneously; the line *appeared again* in the absence of N_2. Analogous experiments with A gave similar results. Increase of

[12] H. Stuart found that oxygen is most effective in extinguishing the resonance radiation of mercury.

[13] Landolt-Börnstein, Tabellen.

pressure from 3.5 up to 52 mm caused an increasing *decay* of fluorescence, while the spectrum *brightened up remarkably as soon as the gas was removed*. This "negative" effect could be obtained over and over again with *gases of the same purity* as those which gave "positive" effects in the simpler tube. It has been noticed, however, that the "negative" effect became less pronounced with time, especially after the tube *was allowed to cool down frequently*. Evidently, the metallic thallium distilled slowly over into the main part of the tube bringing it automatically to the same conditions that existed in tubes used before; and, in fact, when the metal was then transferred in vacuum into the main part of the tube, and the side-tube *s* was sealed off, only the regular "positive" effect appeared again. It is evident, therefore, that as long as we work with "open," not uniformly heated tubes, we actually know nothing about the pressures of the components of the metallic mixture. All assumptions as to the nature of the elementary mechanism of energy transfer with or without the co-operation of atoms in the metastable $2p_3$ state will then necessarily retain a considerable degree of uncertainty.

10. Preliminary experiments had shown that it is not difficult to obtain the sensitized fluorescence of Tl in a *closed tube, heated uniformly* in a furnace. This discovery opened the possibility of a comparison of the intensity of Tl fluorescence in two sealed-off and uniformly heated tubes, one of them containing merely Tl and Hg, the other the same metals in an atmosphere of the gas under known pressure. The pressure of Tl vapor being then determined by the temperature of the furnace, it was only necessary to introduce into the tube a known amount of mercury vapor. It must be emphasized, however, that, according to what has been said before about the processes going on in an "open" tube, while the enhanced fluorescence appears, the pressure of mercury vapor cannot be regarded as known. It was, therefore, necessary to seal off *three* tubes prepared as follows:

The tube *a* connected with the pump and the gas container in the same way as before, was heated up to 680°C, the temperature of the side-tube with mercury being kept at 90°C. Pure N_2 of 5 mm pressure was then introduced into the tube. *While a very strong effect appeared on the green line 5350, the tube was sealed off from the pumps.*

The tubes *b* and *c* were at first connected together and to the pump and put side by side into the furnace. By shifting the illuminating lens a little one could observe the Franck-Cario effect alternatively in each of them in the same way as before. Under the influence of N_2 at 8 mm pressure the green fluorescence appeared exceedingly strong. *The tubes were then allowed to cool down to a temperature of 130°C, and were kept at*

this temperature for two hours, the temperature of the mercury being only 110°C. After two hours one of the tubes *b* was sealed off. The other tube *c* was then pumped out and kept under highest vacuum at 130°C for another two hours and then sealed off from the pumps. The temperature of mercury was all the time kept constant at about 110°C.

Each tube was then examined in a uniformly heated furnace. Visual observations made on the green line λ5350 gave the following results.

Tube a containing Tl vapor at saturation pressure, N_2 at 5 mm, mercury vapor at the pressure $\leqq 0.16$ mm. The Tl line appears at the temperature of 360°C, increases rapidly in intensity with increasing density of the vapor and is at 700°C much stronger than 5461 (always present due to reflection and scattering). There is no difference whatever between the appearance and intensity of the spectrum in this sealed-off tube and the phenomenon observed before in an "open" tube under the same conditions.

Tube b containing Tl at saturation pressure, N_2 at 8 mm, and Hg at 0.5 mm. The line appears at about 410°C, increases in intensity with increasing density of the vapor, but does not reach the same brightness at 700°C as in the tube (a).

Tube c containing Tl at saturation pressure, Hg at 0.5 mm, and no gas. The line does not appear until about 510°C is reached, is remarkably weaker than in *a* and noticeably weaker than in *b*. The appearance and intensity of the spectrum are the same as in open tubes, without gas.

11. Fig. 4 shows the lines 5350, 3776, 3529, 3519, in all three tubes at different temperatures. The comparison of the intensities of the spectra excited in the tubes *a* and *c* shows conclusively that (1) the effect of N_2 on the intensity of sensitized fluorescence of Tl *persists in uniformly heated sealed-off tubes*; (2) it cannot be explained as due to differences in pressure of Tl or Hg, caused by diffusion and condensation in a not uniformly heated "open" tube.

The comparison of the phenomenon in tubes *b* and *c* shows that the effect is due *entirely to the presence of the gas*, thus confirming Franck's hypothesis as to the part the metastable $2p_3$ atoms must take in the elementary act of energy transfer.

Finally, comparing the intensities of the spectra excited in the tubes *a* and *b*, we see that the phenomenon observed for the first time by Donat is very strong when the pressure of mercury vapor is lower (0.16 mm) than that of Tl (0.45 mm), and less pronounced when the pressures of mercury (0.5 mm) and Tl are nearly equal. This seems to indicate that the metastable $2p_3$ atoms *while enduring very many collisions with N_2 molecules or A atoms may not as easily retain their energy in a collision*

with normal mercury atoms. It is, however, possible that the probability of an energy transfer from $2p_3$ atoms to normal mercury atoms is yet much smaller than the probability of a transfer from $2p_3$ atoms to Tl atoms. This is indicated by the fact that the enhancing effect of N_2 could be observed accidentally in a tube containing a minute amount of Tl as impurity.

An attempt has been made to excite the sensitized fluorescence of Ga, but no Ga lines could be detected on the plates after one hour exposure at 960°C. The saturation pressure of Ga being still very low at this temperature it was expected that the presence of N_2 might perhaps sufficiently enlarge the amount of energy available for excitation. The plate obtained after one hour exposure at a temperature of about 960°C with 5 mm N_2 present in the tube did not show any Ga lines, but very weak traces of λλ5350, 3776, 3529, 3519 of Tl appeared distinctly. The tube had been used previously for experiments with Tl and although cleaned very thoroughly before Ga was put in evidently still contained enough thallium as impurity. It must be emphasized that the Tl lines were just detectable *only when* nitrogen was present, and were not to be found in the spectrum obtained with the same tube without gas.

This observation is valuable for two reasons: (1) It confirms the results previously obtained under conditions that exclude the possibility of the effect investigated being due to diffusion or condensation processes. (2) It indicates that the probability of an energy transfer through collisions from $2p_3$ atoms to Tl atoms is very much larger than the probability of such a transfer from $2p_3$ to normal Hg atoms.

The writer wishes to express his best thanks to Professor R. A. Millikan for the opportunity of carrying out experimental research in the Norman Bridge Laboratory, and for his stimulating interest throughout this investigation. He is also indebted to Dr. I. S. Bowen for his valuable assistance in the photographic part of the work.

NORMAN BRIDGE LABORATORY OF PHYSICS,
PASADENA, CALIFORNIA
June 12, 1925.

SCATTERING OF ELECTRONS IN IONIZED GASES

By Irving Langmuir

Abstract

Velocity distribution of electrons in low pressure discharges from hot cathodes.—Analysis of the current received by a collector placed opposite a hot cathode indicates that there are three groups of electrons present; (1) *primary electrons* which retain practically all the momentum they acquired in passing through the positive ion sheath around the cathode; (2) *secondary electrons* moving in random directions with a Maxwellian velocity distribution corresponding to a temperature roughly proportional to the energy of the primaries (200,000° for 100 volt primaries) and approximately independent of the nature or pressure of the gas or the current density; (3) *ultimate electrons* having a Maxwellian distribution of velocities corresponding to a much lower temperature than that of the secondaries, a temperature which is independent of the current density or the voltage of the primary electrons and which varies with the gas used and decreases slowly as the pressure is raised. The number of ultimate electrons is roughly 1000 times that of the primaries and secondaries for mercury vapor, although relatively less numerous in the case of hydrogen. In the uniform positive column of arcs only ultimate electrons are present.

The velocity distribution of the primary electrons may be resolved into a drift velocity normal to the cathode surface and a random motion with a Maxwellian distribution corresponding to a temperature which varies approximately with the square of the current and is a maximum at a mercury vapor pressure of about 0.6 bar, falling to a low value at 8 bars, and is considerably higher with 35 volts accelerating potential than with 80 volts. Under favorable conditions with 40 mil-amp. this temperature may rise to 80000° and there are then appreciable numbers of these primaries which can reach a collector charged to a potential as much as 40 volts below that of the cathode. Experiments with two crossed electron beams prove that the secondary and ultimate electrons, directly or indirectly, are responsible for very little if any of the scattering.

A study of the ultimate electrons in the positive column of a low voltage mercury arc shows that the Maxwellian velocity distribution corresponding to a high temperature (30000°) is maintained in a small tube in spite of the fact that the negatively charged walls of the tube constantly tend to disturb this distribution by selective removal of the faster electrons. The number of collisions of the electrons with each other and with atoms were far too few to maintain the observed distribution. Measurements of the mobilities of electrons in arcs and of the electron concentration differences produced by a transverse magnetic field gave values for the mean free path only 1/10 as great as the values determined by a direct method. These results all indicate that the electrons in low pressure arcs suffer many changes of momentum during the time intervals between successive collisions between atoms, ions or electrons.

Mechanism of electron scattering.—After analyzing the effects to be expected when a beam of primary electrons encounters a cloud of stationary electrons or a cloud of particles of small mass but of high temperature, it appears that the experimental results for the ratio of the scattering to the average retardation of

the beam was best accounted for by collisions with a cloud of radiation quanta, a kind of Compton effect. The observed scattering is, however, about 10^{14} times greater than a normal Compton effect would give It is suggested that the joint action of excited atoms and radiation may multiply the Compton effect sufficiently, or it may be that the presence of a free electron within a distance of a wave-length from an excited atom may greatly increase the probability of a quantum jump and that momentum is delivered to the electron in the process. In arcs the ultimate electrons may be in a kind of thermal equilibrium with radiation and excited atoms.

Scattered electrons in high vacuum.—In connection with a study of the Barkhausen-Kurz effect and in a magnetron with negatively charged end plates, evidence of the presence of electrons with abnormally high speeds has also been obtained. These have been explained as due to electric oscillations, but the effects have also been obtained when oscillations are not present. This seems to indicate that electron scattering similar to that observed in low pressure gases can also occur in high vacuum.

I. Electrons in the Positive Column of Low Voltage Arcs

Distribution of velocities. By studying the volt-ampere characteristics of small electrodes or collectors placed in the path of an arc in mercury vapor at low pressures, it has been found[1,2] that the free electrons in the arc are moving in nearly random directions with velocities which are distributed quite accurately in accordance with Maxwell's distribution law.

When the collector is at large negative potentials with respect to the surrounding gas, it receives only positive ions, but at higher potentials (algebraically) electrons also are collected. At first only electrons of the highest velocities are able to reach the collector against the retarding potential, but as the potential is raised, making the retarding field weaker, electrons of lower velocity can be collected. If the velocities of the electrons are distributed according to Maxwell's law, the logarithm of the electron current flowing to a negatively charged collector should be a linear function of the potential of the collector, with a slope (when plotted using natural logarithms) of e/kT, where T is the temperature corresponding to the electron velocities and e/k has the value 11600 degrees per volt.

When the collector is made positive with respect to the surrounding gas the electron current increases with the potential more slowly and according to entirely different laws. Thus the semi-logarithmic plot of the current-voltage characteristic should be a straight line only for negative voltages and a kink therefore should occur in the curve at a point at which the potential of the collector is the same as that of the

[1] Langmuir, Jour. Frank. Inst. **196**, 751 (1923).
[2] Langmuir and Mott-Smith, Gen. Elec. Review **27**, 449, 538, 616, 762, 810 (1924).

surrounding gas. By this method collectors may be used to measure the true space potentials.

When a small plane collector is at the space potential in an arc in mercury vapor, the electron current is about 400 times as great as the positive ion current which flows when large negative voltages, sufficient to repel all electrons, are used. Thus, if the collector is disconnected (or is allowed to "float") it charges itself negatively with respect to the surrounding gas until it is able to repel 399/400^{ths} of all the electrons which move towards it, the electrons and positive ions then being collected in equal numbers. Experiments with mercury vapor, hydrogen, nitrogen, argon and neon at low pressures have shown that the semi-logarithmic plots for negative voltages are usually surprisingly straight over very wide ranges of current. The straight semi-logarithmic plot of the electron current extends to negative voltages far beyond that to which the collector charges itself when it is floating. For example, the straight plot was easily observed down to currents only 1/6000th of the total current.[3] A. F. Dittmer working with Karl Compton at Princeton has recently found, using an improved method by which positive ions and electrons are separated, that with a 40 milli-ampere arc in nitrogen at 8 bars pressure, the straight line plot extends down to current densities of less than 10^{-5} of the total current density. The electron temperature in this case was about 50000°.

The electron temperatures corresponding to these straight plots are practically independent of the current densities in the arcs, but increase as the pressure is lowered. For example, currents of from 0.1 to 5 amperes in a tube 3 cm in diameter gave electron temperatures of about 30000° with mercury vapor at 1 bar; 20000° at 5 bars, and 10000° at 30 bars. With other gases the electron temperatures are usually higher.

If thermal equilibrium existed in the ionized gas the electrons would of course have a Maxwellian distribution of velocities corresponding to the temperature of the gas. If this distribution is disturbed by any external cause it tends to re-establish itself through the agency of every mechanism by which electron velocities can be modified. For example, collisions of electrons with each other, with atoms or excited atoms, or the interaction of electrons with the black body radiation, will all tend to bring back the Maxwellian distribution of the electrons. The rate of re-establishment of this distribution would be different for each mechanism if that alone were allowed to act. Corresponding to each mechanism we may therefore conceive of a "time of relaxation" which is the time

[3] See, for example, Fig. 1 in Gen. Electric Rev. article (loc. cit.[3]), p. 451.

that would be needed for any disturbance in the Maxwellian distribution to fall to $1/e^{th}$ of its value, if only the one mechanism were effective.

We will consider first the interaction between atoms and electrons. The mercury atoms which strike the walls of the tube deliver their surplus energy and leave the glass with a kinetic energy corresponding to room temperature. For mercury vapor at 1 bar and a temperature of 300°K, there are 2.4×10^{13} atoms per cm³. Measurements with collectors in a 2 amp. arc in a 3 cm tube have shown that there are 8×10^{10} free electrons per cm³. In this case the average distance an atom will travel before colliding with an electron is 1.5 cm and in a tube 3 cm in diameter it will make only about four collisions with electrons between consecutive collisions with the wall. Taking the temperature of the electrons as 30,000°, the mercury atom gains on the average only 0.08° at each collision. Thus the temperature of the mercury vapor which strikes the walls will be only 0.3° above the temperature of the walls. This at least represents the temperature that can be acquired by direct interaction with the electrons. Of course there will be a minute fraction of mercury atoms which collide with excited mercury atoms and thus acquire very high kinetic energy, but we may ignore these at present. The time of relaxation corresponding to the interaction between electrons and atoms by collisions is thus at least 100,000 times too great to be effective in bringing about temperature equilibrium and thus affording a means of maintaining a Maxwellian distribution for the electrons.

Since the normal free path λ_e of electrons under the conditions considered, is 30 cm, it is clear that the average distance an electron would have to travel before colliding with an excited atom would be much greater than this and therefore collisions of the second kind, in the ordinary meaning of this term, cannot be responsible for bringing about the electron velocity distribution. The same may be said of collisions of electrons with each other. The concentration of electrons is only $1/300^{th}$ that of the atoms and if we assume the target area of an electron is the same as that of an atom, the average distance that an electron would move before colliding with another electron would be 6400 cm (allowing for the velocity of the electron being struck). A careful calculation has been made, based on Coulomb's law, of the effect of the electric force between the electrons in increasing the transfer of momentum by collisions. It is found that the effective free path varies with the electron velocity, but that the free path is still so great that this kind of interaction between electrons must be completely rejected as a possible mechanism for bringing about the observed Maxwellian distribution.

Effect of the charged glass walls. The glass walls of the discharge tube are negatively charged because of the fact that the electron current density in the discharge is greater than the positive ion current density. In accordance with observation we may take the electron current in mercury vapor to be 400 times the ion current. If the electron temperature is 30,000° it can then be calculated (in agreement with experiment) that the walls will be charged to -15.5 volts with respect to the ionized gas and will thus be covered by a positive ion sheath. All electrons which have energy components normal to the surface of the glass of less than 15.5 volts will be specularly reflected from the walls without loss of energy, but electrons having energy components greater than this will pass through the sheath and be taken up by the walls except for the few that are reflected back. Thus the walls are continually disturbing the Maxwellian distribution by removing the high speed electrons. We should therefore expect distinct departures from a straight line semi-logarithmic plot at collector voltages below that to which the glass walls become charged, unless there is a mechanism which effectively re-establishes the Maxwellian distribution within a distance less than that which separates the collector from the opposing glass walls.

In the experiments made by Harold Mott-Smith Jr. and the writer with mercury arcs in a tube 3 cm in diameter,[4] the collector which was designated *H* consisted of a square nickel plate 1.9 cm on a side which had been bent into a cylindrical surface which conformed to the inner surface of the tube. If electrons traverse the tube in straight paths with constant velocity and are specularly reflected from the cylindrical walls, the radial velocity components in successive collisions with the walls remain constant. If then the walls of the tube are negatively charged to say -15.5 volts *few electrons can reach a cylindrical collector such as H, with radial components greater than 15.5 volts unless these electrons have acquired this large radial velocity within the distance they have travelled since their last collision with the wall.*

The experiments showed in all cases that the straight semi-logarithmic plot extended to negative voltages far below those to which the collector *H* charged itself when it was allowed to float. This must be taken as proof that the higher velocity electrons were produced from low velocity electrons while these travelled a distance of less than 3 cm.

From the complete absence of a kink in the semi-logarithmic plot at the wall potential we must conclude that the time of relaxation corresponding to the mechanism by which the electrons acquire their Max-

[4] Loc. cit[2], p. 538.

wellian distribution is small compared to the time taken for the electrons to traverse the tube, in other words, that the free path of the electrons corresponding to this mechanism is small compared to 3 cm.

Effect of charged conducting walls. Recently Mott-Smith has carried out experiments with a mercury arc at low pressures passing through a metallic cylinder split lengthwise into two halves, which are insulated from one another. One half was used as a collector while the other was maintained at a series of different negative voltages to see if the velocity distribution of the electrons reaching one electrode was modified in any way as different groups of electrons were removed by means of the opposite electrode. It was found in fact that by charging one electrode so strongly negative that even the high speed electrons were reflected from it, the temperature of the electrons collected by the opposite half-cylinder was distinctly higher than if the electrode were at only -15 volts with respect to the gas so that all the higher speed electrons were removed. *But in both cases a perfectly straight semi-logarithmic plot was obtained.* The removal of the high speed electrons lowered the temperature, but the Maxwellian distribution was established while the electrons moved between the two collectors. Experiments are now in progress by A.F. Dittmer using plane collectors whose distance apart can be varied, to determine directly the rate at which the Maxwellian distribution is brought about.

Evidence as to the mean free path of electrons.[5] If a small potential gradient dV/dx is allowed to act on electrons having a Maxwellian velocity distribution, the electrons drift in the field with an average velocity v_x given by the mobility equation

$$v_x = 4\gamma\lambda/\pi v \tag{1}$$

where γ the acceleration of the electrons is

$$\gamma = \frac{e}{m}\frac{dV}{dx}, \tag{2}$$

λ is the mean free path of the electrons and v is the average velocity of the electrons (assumed to follow Maxwell's law). Expressing v in terms of T_e and inserting the value of e/m we get

$$v_x = 3.62\times10^9 \cdot \frac{\lambda}{\sqrt{T_e}}\frac{dV}{dx} \tag{3}$$

where v_x, λ and x are expressed in cm-second units and V is in volts.

[5] A brief note on the abnormally small values of the free paths of electrons obtained from the mobility and from the effects of transverse magnetic fields was given in the last paper by Langmuir and Mott-Smith, loc. cit.[2], p. 819.

The current density I_x of the arc is related to v_x by the equation

$$I_x = n_e e v_x$$

or if I_x is in amp. per cm^2

$$I_x = 1.59 \times 10^{-19}\ n_e v_x. \tag{4}$$

Combining these equations

$$I_x = 5.76 \times 10^{-10} \frac{n_e \lambda}{\sqrt{T_e}} \frac{dV}{dx}. \tag{5}$$

With the 2 ampere arc in mercury vapor at 1 bar in a tube 3.2 cm in diameter the current density I_x was 0.25 amp. per cm^2, $n_e = 8 \times 10^{10}$, $dV/dx = 0.25$ volts per cm, and $T_e = 30{,}000°$. Substituting these into Eq. (5) and solving for λ we find that the free path λ of the electrons in the arc is 3.8 cm. Direct measurement of the number of 50 to 250 volt electrons which pass through ionized mercury vapor at 1 bar without collision with atoms, give a free path of at least 30 cm. The recent investigations of Ramsauer and others, show that for lower velocities (below those necessary to produce ionization), the free paths tend to increase. A large number of measurements of λ with arcs in mercury vapor at various pressures, in tubes of various diameters and with a wide range of current densities have been made in this laboratory. The free path calculated from the mobility always comes out to be 5 to 10 times lower than can be reconciled with direct determination or with values calculated by the usual methods of the kinetic theory.

The application of transverse magnetic fields of 50 to 100 gauss to a mercury arc at low pressures causes the arc to be deflected to one side. By measuring the *ratio of the electron concentrations* at two points along a diameter of the tube which is perpendicular to the magnetic field, it is possible to calculate the free path by a method entirely independent of that involving the mobility. This method also gives free paths about 10 times smaller than the distances which electrons travel before colliding with atoms as obtained by direct measurement.

Both of these results as well as the rapid establishment of the Maxwellian distribution of electron velocities, suggest that *the electrons in a mercury arc suffer many changes in momentum during the time that elapses between consecutive collisions with atoms.*

Summary. This discussion of the results obtained from a study of low pressure arcs shows (1) that the free electrons have velocities with a Maxwell distribution corresponding (in the case of mercury vapor at 1 bar) to a temperature of 30,000°; (2) that this distribution is maintained even when the walls are negatively charged and hence are constantly removing the faster electrons; (3) that the number of collisions with

atoms and electrons is far too small to maintain this distribution, the mean free path being of the order of the tube diameter; (4) that mobility experiments indicate that the electrons suffer at least ten changes of momentum between consecutive collisions with atoms. A possible explanation of these results will be presented and discussed in Part IV below.

II. Electrons Accelerated from a Hot Cathode

These Maxwellian distributions occur not only in ordinary low pressure arcs but are produced in gaseous discharges under many different conditions. We will now consider some experiments which have been made with spherical bulbs or cylindrical vessels containing a hot tungsten cathode and a disk-shaped anode. With gases at low pressures, currents of the order of ten milli-amperes and anode potentials of 50 to 250 volts, the space potential in the strongly ionized gas is nearly uniform and is somewhat above that of the anode. The cathode is surrounded by a positive ion sheath in which there is a sharp potential drop so that the electrons from the cathode are accelerated within a distance of a fraction of a millimeter, to a velocity exceeding that which corresponds to the potential difference between the anode and cathode.

Recently a very large number of experiments have been made by S. P. Sweetser, C. G. Found and H. A. Jones to investigate the production of these high speed electrons. A brief report of this work was made at the April meeting of the Physical Society[6] in Washington.

In one set of experiments (Exp. 548) a straight tungsten filament 1.1 cm long and 0.18 mm in diameter was mounted within about 2 cm of the center of a spherical bulb of 12 cm diameter. A disk-shaped collector 1.1 cm in diameter, backed by mica and movable in the direction of its axis, was mounted so that the axis passed through and was perpendicular to the filament at its center. The lead to the disk was insulated so that the collector could receive electrons only on the surface facing the filament. An anode was also placed in the bulb to one side of the line connecting the other electrodes.

By lighting the filament so that it emitted 5 milli-amperes and applying -50 volts to the cathode with respect to the anode (assumed to be at zero volts) the mercury vapor became strongly ionized and its potential was nearly uniform and equal to that of the anode. The electrons emitted by the filament acquired their full velocity within a few tenths mm and were therefore projected outwards in directions normal to the filament, thus forming a disk shaped "beam" of electrons. Those electrons

[6] Langmuir, Abstract in Physical Review **25**, 891 (1925).

which reach the collector with a large part of the momentum which they acquired in passing through the positive ion sheath, we shall call *primary electrons*. The primary electrons in this beam which were intercepted by the collector were moving perpendicularly to its surface. To prevent these electrons from reaching the collector it was necessary to apply a potential lower than that of the cathode.

Thus, as the collector passed through the potential of the cathode, the current-voltage curve of the collector showed a sudden change in current which was a measure of the number of primary electrons which reached the collector without collisions. This discontinuity was very sharp when the cathode emission was only 5 m-amp. taking place within a range of only about 2 volts, which was not greater than would be expected because of such effects as the initial velocities of the emitted electrons and the voltage drop along the filament. Thus no appreciable number of electrons were present in the gas with velocities higher than those of the primaries.

Scattering of primary electrons. When the electron emission was raised to 10 m-amp. however, there were found to be unmistakable indications of the presence of electrons having velocities higher than the original primaries. Fig. 1 shows some typical data taken with 10 m-amp., with a cathode potential of -50 volts, and a distance of 3 cm between filament and collector. The mercury vapor pressure was only 0.23 bar corresponding to saturated vapor at 0°C. The curve marked I_b gives the collector current in micro-amperes as a function of the collector potential. The curves 0.1 I_b and 0.01 I_b represent the same data on a scale 10 and 100 times smaller so as to bring the upper portions of the curve within the plot.

It is seen that at collector potentials below -60 only positive ions are collected. The currents vary with the potential because of an "edge correction" which causes[7] the area of the positive ion sheath to increase as the sheath thickness increases. The dotted line A shows how this current would vary at higher potentials if no electrons were collected. At potentials above -59 volts, at point M, electrons begin to be collected, showing the presence of appreciable numbers of electrons having energies of from 52 to 59 volts although the energy of the primaries was only 50 volts.

From the data of Fig. 1 we see that with the collector at -40 at point N practically all the primaries have been collected. With a cathode current of only 5 m-amp. on the other hand, the primaries were all collected with voltages of about -47. This shows that the effect of raising the primary current from 5 to 10 m-amp. was to scatter the primary electrons,

[7] See loc. cit.[2], p. 540.

causing not only an increase in the velocities of some of the primaries but a decrease in the velocity of others. The average energy of all the primaries was slightly lowered to about 47 volts. The total number of primary electrons collected was twice as great with 10 as with 5 m-amp. cathode current, so that the effective free path of the injected electrons remained

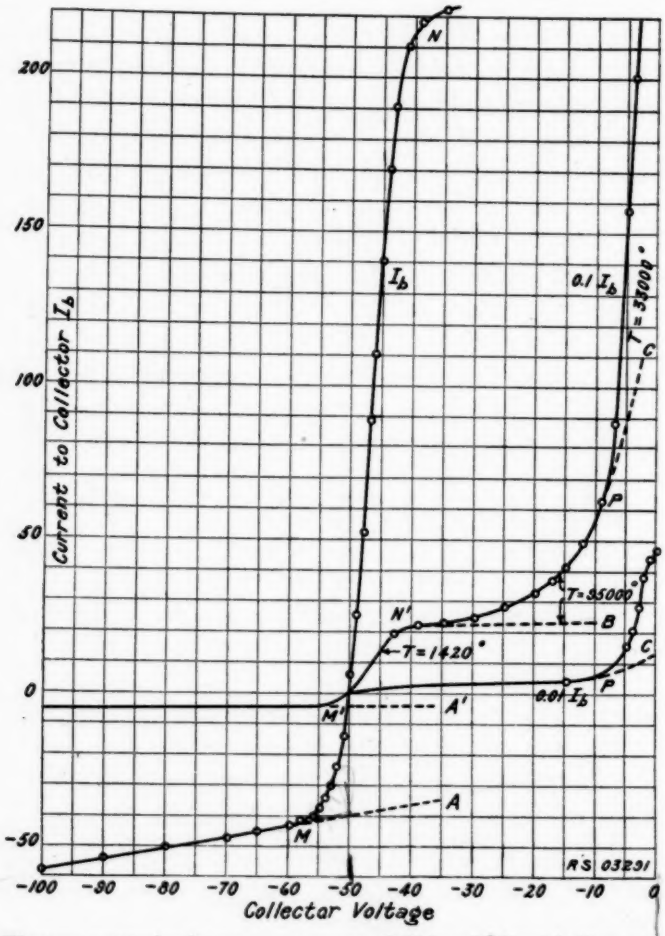

Fig. 1. Electron scattering in mercury vapor at 0.23 bar (0°C) with 10 m-amp. primary current and the cathode at −50 volts.

the same, if by free path we mean the distance that the electrons travel before losing the greater part of their momentum in their original direction.

By subtracting from the observed currents (Fig. 1) the positive ion currents corresponding to the dotted line A we obtain the total electron current ΔI_b to the collector. In Fig. 2 the logarithms of these currents in

micro-amperes have been plotted against the collector voltage. In this way the data for from −55 to 0 volts are brought within a single convenient curve. The rise MN which occurs between −55 and −40 volts corresponds to the primary electrons. If these all had the original energy of 50 volts the rise should occur as a vertical line at an abscissa of −50 volts. The inclination of the line from the vertical thus measures the amount of electron scattering.

The line $N'B$ in Fig. 1, corresponding to the horizontal dotted line NB in Fig. 2, gives the current as it would be if no other electrons than the primaries were collected. The differences between the observed currents $N'P$ and those of line $N'B$ (Fig. 1) thus correspond to a new group of electrons which probably result from collisions of the primary electrons with gas molecules. We shall call these *secondary electrons*. This group includes primaries which have lost most of their energy and also electrons which are ejected from gas molecules by these collisions.

The distribution of velocities among the secondary electrons is found by taking the differences between the observed currents and the current corresponding to $N'B$ (Fig. 1), and by plotting the logarithms of these differences as indicated by the points along the line D (Fig. 2). Within the range from −30 to −12 volts the points lie on a straight line. This proves that the velocity distribution follows Maxwell's law. From the slope the temperature of this secondary electron group is found to be 95,000°. By extrapolation to higher voltages along the straight line D, the currents corresponding to the secondary electrons are calculated as indicated by the dotted line PC. Thus the line NPC is the curve of the secondary electrons.

The difference between the observed currents PR and the secondary currents PC (Fig. 1) gives another group of electrons which we will see have a Maxwellian velocity distribution and are in fact the same as the free electrons found in the positive column of the low voltage discharge. We shall call these the *ultimate electrons*. If the currents due to these are small compared to the current flowing to the anode the logarithms of the currents may be plotted and the slope of the resulting straight line taken to measure their temperature. But, it often happens that the concentration of the ultimate electrons is so high that the current taken by the collector becomes comparable with that flowing to the anode. The collector may, in fact, rob the anode of nearly all its current and thus raise the space potential along with the collector potential. In these cases, as mathematical analysis shows, we should plot the logarithm of the ratio of the electron current to the collector, to the current to the anode. The slope of this line as indicated by line E measures

the temperature of the ultimate electrons. In view of the logarithmic scale of Fig. 2 it will be seen that the number of ultimate electrons greatly exceeds that of the primary or secondary electrons. The relative numbers of electrons in the various groups is seen more clearly in Fig. 1 because there the currents themselves are plotted as ordinates. The dotted lines $N'B$ and PC on Fig. 1 are drawn to correspond to those in Fig. 2.

In other experiments disk-shaped collectors were mounted close to the primary electron beam but in a plane perpendicular to the axis of the cathode so as to be parallel to the direction of the electron beam. The current to such a collector gives no indication whatever of the prim-

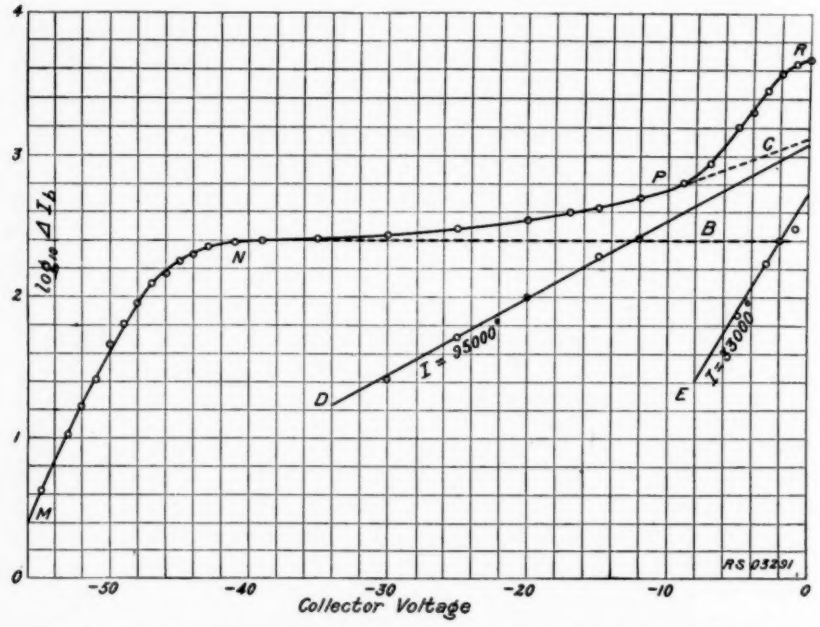

Fig. 2. Semi-logarithmic plot of the electron currents from the data of Fig. 1.

ary electrons corresponding to the rise MN, but the groups of secondary and ultimate electrons corresponding to the rises between NP and PR are exactly the same as those shown in Fig. 2 for a collector mounted perpendicular to the beam. Such experiments justify our separation of the electrons into groups of primaries and secondaries and establish the fact that the primaries move mainly in one direction while the secondaries and ultimate electrons move equally in all directions.

In our present discussion our interest centers on the *distribution of the velocities of the primary electrons* after they have passed through the ionized gas. The portions of the curves MN in Figs. 1 and 2 should give

us this distribution. In order to analyze such curves mathematically the hypothesis was made that the scattering of the primaries takes place in such a way that the resultant velocity distribution can be analyzed into a uniform translational velocity and a superposed Maxwellian distribution corresponding to a temperature T—this distribution being analogous to that of the molecules of a gas which is moving with uniform velocity.

We can now calculate what fraction of the electrons in such a beam can move against a given retarding field like that in the sheath of a negatively charged plane collector. Assuming that the velocities due to temperature motion are small compared to those of translation it can be shown that the current I of electrons which reaches a collector is given by

$$I=\tfrac{1}{2}I_0(1+\operatorname{erf}\beta) \tag{6}$$

where erf denotes the error function

$$\operatorname{erf} x=\frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}dx\,. \tag{7}$$

I_0 is the current when all the primary electrons are collected and β is defined by the equation

$$\beta=(\sqrt{-V}-\sqrt{V_1})/\sqrt{V_T}. \tag{8}$$

Here V is the potential of the collector with respect to the ionized gas (or anode), V_1 is the potential corresponding to the translational velocity of the primary electrons and V_T is the potential corresponding to the energy kT, k being the Boltzmann constant. If V_T is expressed in volts

$$V_T=T/11600. \tag{9}$$

When the collector potential is not too far from that of the cathode the value of β from Eq. (8) may be expanded giving

$$\beta=\text{const}+V/(2\sqrt{V_1V_T}). \tag{10}$$

Thus β is a linear function of the collector potential and from Eqs. (6) and (10) we then see that $\operatorname{erf}^{-1}[(2I-I_0)/I_0]$ is a linear function of V having a slope equal to $1/(2\sqrt{V_1V_T})$. If this function of I is plotted against V and a straight line is obtained it proves the existence of the kind of velocity distribution we have assumed, and enables us to determine the temperature corresponding to the random part of the motion. These operations may be more conveniently carried out by using probability paper in which the vertical lines are uniformly spaced and the horizontal

lines, which are denoted by various values of a parameter a, are spaced according to the relation

$$y = \text{erf}^{-1}(2a-1)$$

Temperature of primary electrons. In Fig. 3 the primary electron currents corresponding to the data of Figs. 1 and 2 are plotted on probability paper. The abscissas are the collector voltages while the ordinates are $\Delta I_b/I_0$ where I_0 has been taken as 257 micro-amperes in accordance with the data of Fig. 1. It is seen that the observed points lie very close

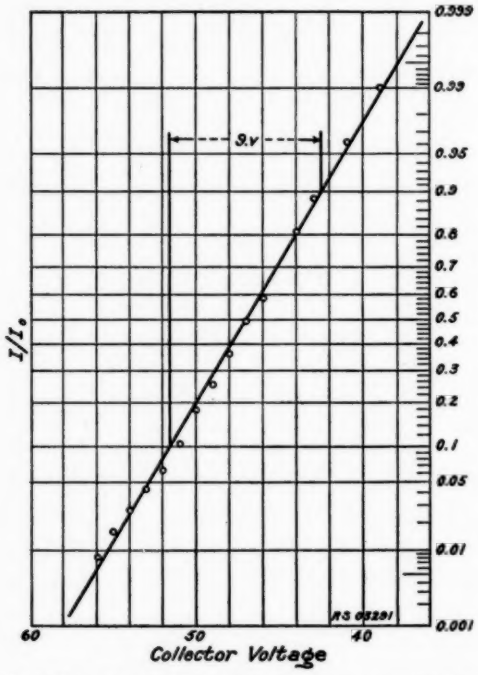

Fig. 3. Probability plot of the primary electron current from data of Fig. 1.

to a straight line. The difference in voltage corresponding to the 2 points $I/I_0 = 0.1$ and 0.9 is 9.0 volts. The increment of $\text{erf}^{-1}(2a-1)$ corresponding to these values is 1.812. Thus by (10)

$$dV/d\beta = 9/1.812 = 2\sqrt{V_1 V_T}.$$

Since the energy of the primary electrons in the beam corresponds to 50 volts we place $V_1 = 50$ and thus find $V_T = 0.122$ volts or by (9) $T = 1420°$. The voltage on the probability plot (Fig. 3) which corresponds to the midpoint (i.e. where $I/I_0 = 0.5$) measures the average translational velocity of the electron beam. Thus from Fig. 3 the forward velocity of the

beam corresponds to 47.2 volts although the original velocity of the primary electrons corresponded to 50 volts. The mechanism producing the scattering therefore does not act uniformly in all directions but produces the greatest changes in momentum in a direction opposite to that of the original beam.

The data from large numbers of experiments, of which the data of Fig. 3 are typical, confirm the correctness of the hypothesis that the primary electrons have random Maxwellian velocities superposed upon the translational velocity. The degree of scattering in this case is very small as the voltage corresponding to the random velocities is only 0.122 while the voltage of the translational velocity is 47.

Variation with current density. To illustrate the effects produced by modification in the experimental conditions we may consider another typical run made with the same apparatus. The pressure of the mercury vapor was 1.6 bars corresponding to saturated vapor at 20°C. The electron emission from the cathode was 30 m-amp. The cathode was at a potential of -50 volts with respect to the anode, and the distance from the collector to the cathode was 3 cm as in the run illustrated in Figs. 1 to 3. The data were plotted and analyzed as before. Appreciable electron currents were observed with collector potentials as low as -90 volts showing that some electrons (about 3 micro-amperes) having energies as high as 90 volts had been produced from the original beam of 50 volt electrons. The secondary electrons gave a straight semi-logarithmic plot corresponding to $T=95{,}000°$ which is the same temperature as found from the data of Fig. 1. The temperature of the group of ultimate electrons was 15,600°. The plot of the primary electron current to the collector, on probability paper, gave 17 consecutive points in the voltage range from -90 to -10 volts which came very close to a straight line (maximum departure 3 volts) whose slope corresponded to $T=56{,}000°$. The mid-point of this line was at -36 volts so that the beam had been retarded by an amount corresponding to 14 volts.

The very much higher temperature of the primary electrons in this experiment as compared to the previously described run is due mainly to the higher primary current density, but is partly due to the higher pressure of mercury vapor.

Fig. 4 illustrates the current-voltage curves of the collector for potentials below that of the cathode with a series of different primary current densities. The figures written near the curves are the electron emissions from the cathode in milli-amperes. Three different cathode potentials were used, -35, -50 and -70 volts. The actual experimental points

are indicated in only one curve, which being typical, illustrates the accuracy with which the observations fit the curves.

The moderately sloping parts of the curves, which are continued as dotted lines to the right, give the positive ion currents. The departures from these lines measure, as before, the primary electron currents. It will be noted that with 5 m-amp. the electrons begin to be collected only when the collector comes within 1 or 2 volts of the cathode potential, showing that there are very few electrons having higher velocities than those of the original primaries. As the current density is increased to

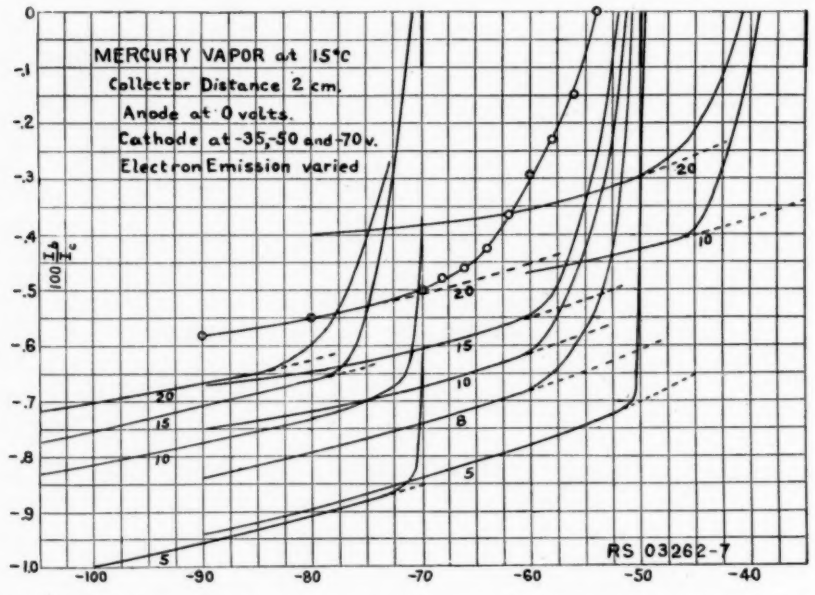

Fig. 4. The effects of cathode voltage and current density on the scattering of electrons. The ordinates give the ratio I_b/I_e where I_b is the negative current received by the collector and I_e is the electron emission from the cathode. The figures marking the curves are the values of I_e in milliamperes.

10 or 20 m-amp. however, electrons begin to be collected at potentials of 10 or even 20 volts below that of the cathode. The effect seems to be somewhat more marked at 35 and at 50 volts than at 70 volts.

In a series of later experiments the primary electron temperatures were determined for each of a series of primary current densities corresponding to electron emissions ranging from 3 to 30 m-amp. The mercury vapor pressure was 0.23 bars (0°C), the collector distance 3 cm, and the cathode potential -50 volts. The primary electron temperature was found, within the experimental error, to be proportional to the 2.2 ± 0.2 power of the current.

Variation with the distance of the collector. Experiments in which different distances between the cathode and the collector were used have shown that the primary electron temperatures increase roughly in proportion to the distance traversed by the electrons. Further experiments on this effect are in progress.

Variation with cathode voltage. In a series of experiments with mercury vapor at 0.23 bar (0°C) with a collector distance of 3 cm and a current of 10 m-amp. the primary electron temperatures varied with the voltage as follows:

voltage:	−80	−70	−50	−40	−35
T:	800°	900°	1300°	1700°	2200°

With 20 m-amp. current, the other conditions being the same, the temperatures were

at −80 volts	at −50 volts
2050°	4750°

The greatest scattering of the electrons thus occurs at the lowest voltages, but, in general it is difficult and unsatisfactory to work with voltages below 50 volts because the effects of the scattering then tend to be masked by the secondary and ultimate electrons. As the voltage difference between cathode and anode decreases not only does the velocity of the primary electrons decrease but the character of the excitation of the ionized gas may change. For example, with higher voltage, atoms may be excited to higher energy levels. These experiments do not enable us to determine which of these factors is responsible for the change in the amount of scattering.

TABLE I

Effect of mercury vapor pressure on electron scattering.

Primary current (m-amp.)	Mercury Temp.	Mercury Pressure (bars)	Electron temperature	Retardation (volts)	$\frac{\Delta E_1}{\Delta E_r}$
10	0°	0.23	1360°	3.1	17.6
	20	1.6	870	2.3	20.4
	30	3.7	240	1.8	58.
	40	8.0	140	1.4	77.
20	0	0.23	5500	5.0	7.0
	5	0.37	7100	4.5	4.9
	10	0.61	9800	4.8	3.8
	15	1.0	5900	3.5	4.6
	20	1.6	4000	3.2	6.2
	35	5.5	750	1.8	18.5

Variation with mercury vapor pressure. Table I shows the way that the electron scattering varied with the vapor pressure of mercury. The cathode was at −50 volts and the collector distance was 3 cm. The last

column gives the retardation of the beam or the decrease in the translational energy of the beam as determined from the voltage of the mid-point of the straight line on the probability plot.

Experiments with crossed beams. The fact that the electron scattering is negligible at low current density and increases rapidly at higher currents suggests that it is caused by the action of radiation or by excited atoms or ions. To gain more information as to the effect of ionization and excitation of the gas a spherical bulb (12 cm in diameter) was provided with two straight cathode filaments, A and B, each 1.1 cm long, mounted in the same plane at right angles to each other. Facing these cathodes at distances of 4 cm there were disk-shaped collectors (A' and B') of 1.1 cm diameter, the axes of these disks being in the same plane as the two cathodes.

By lighting only one cathode, A, a single disk-shaped beam of primary electrons (about 1 cm thick) was produced. The two collectors A' and B' being about the same distance from the center of the bulb, received the same number of secondary and ultimate electrons, but since B' was outside of the beam (and its surface was parallel to the direction of the beam) only the collector A' received primary electrons.

When both cathodes were lighted the volt-ampere characteristics of the two collectors gave the amount of scattering of each of the two perpendicular electron beams, and thus made it possible to determine the influence of one electron beam on the other.

It was found that the temperature and the number of both the *secondary* and the *ultimate* electrons were always very nearly the same for both collectors whether or not the collector was in the beam of primaries. The temperatures of both these groups were independent of the currents from the cathodes. The number of electrons in each of the 2 groups was a function of the sum of the currents emitted by the two cathodes and was in fact approximately proportional to this sum. Thus it was immaterial whether one cathode emitted 20 m-amp. while the other emitted none, or each of the cathodes emitted 10 m-amp.

The behavior of the primary electrons was entirely different. The total number of primaries that could be received by each of the two collectors was of course proportional to the electron emission of the opposing cathode. If the scattering of the primary electrons were due to the free electrons, or ions, or to the kind of excited atoms and radiation that is produced by the secondary and the ultimate electrons, we should expect that the temperatures of the primary electrons should be determined by the temperatures and the concentrations of these two groups of electrons.

Thus the temperatures of the primaries should also be a function of the sum of the emissions from the two cathodes.

The experiments showed, however, that the primary electron temperature depended mainly on the emission of electrons from the cathode which opposed the collector and was usually only slightly influenced by the emission from the other cathode.

For example, in some runs with mercury vapor at 0.75 bar (12°C) with both cathodes at −80 volts, cathode A was heated to such a temperature that it emitted 5 m-amp. while B was adjusted to emit 20 m-amp. The temperature of the primaries reaching A' was 800° while those reaching B' had a temperature 5200°. When cathodes A and B were at the same temperature and each emitted 20 m-amp., the temperatures of the electrons received by each collector was still about 5000°. By then turning off the heating current to one of the cathodes, say A, so that its emission fell to zero, the temperature of the electrons received by the collector B' facing the other filament was practically unchanged notwithstanding the fact that the concentration of the secondary and ultimate electrons and of the positive ions throughout the whole space in the bulb, fell to about half value.

With mercury vapor pressures corresponding to 20° and especially to 30°C one beam of primary electrons seemed to be able to cause a distinct increase in the temperature of the other beam (which it intersected for about 1/4 of its length). For example, at 30° and with both cathodes at −80 volts but only one cathode lighted so as to emit 20 m-amp., the electron temperature observed at the opposing collector was 700°. By allowing the other cathode also to emit 20 m-amp. both beams of primaries gave a temperature of 2500° thus showing a marked increase in temperature caused by the other beam. However, if one cathode was heated to emit 40 m-amp. while the other was cold the temperature of the beam was 20,000° or 8 times as high as when each cathode emitted 20 m-amp., although the concentrations of the secondary, and ultimate electrons was the same in the two cases. Evidently with mercury at 30° the exponent of the power of the current with which the electron temperature increases is higher than it is with vapor from mercury at 0°C.

From these results we may draw the definite conclusion that the main cause of scattering of 80 volt electrons, especially at low pressures of mercury vapor, is not the ionization, excitation or radiation produced by, or characteristic of the secondary or the ultimate electrons, but the scattering must be due to a more direct effect of the primary electrons and one which is confined to the region actually traversed by these primary electrons. This indicates that the scattering cannot be due to

electrons or ions per se. It leaves open, however, the question as to whether radiation or excited atoms may be the cause. Thus 80 volt primary electrons are capable of exciting mercury atoms to energy levels far above those obtainable from the secondary or the ultimate electrons, and radiations of correspondingly high frequency are similarly produced. Excitation and radiation of this kind might well be confined to the region traversed by the primaries and might thus explain the results of the experiments. The distinct but slight effect of one beam of electrons on the other would then be due to the action taking place within the region (about 25 percent of the total path) where the two beams intersect. Experiments are now in progress to study parallel beams and beams with intersect over nearly their whole lengths in order to clear up this question.*

In some other experiments an arc of 0.2 to 0.5 ampere was passed through mercury vapor in a 12 cm bulb from an external mercury cathode while the distribution of the velocities of 50 volt primary electrons from a hot cathode in the bulb was studied. It was found that the ionization due to the arc did not increase the primary electron temperatures.

III. Mechanism of Electron Scattering

Before taking up this general problem, let us enquire whether the scattering of the electron beam can be due to encounters with other electrons. Since the electrons in the beam start out from the cathode with the same velocity, they have no velocity with respect to one another and therefore cannot deliver energy to one another by collision. Space charge due to the electrons in the beam is neutralized by positive ions, but even if it were not, the electric field due to space charge could produce only transverse scattering and would not change the longitudinal velocities of the electrons.

Scattering by clouds of stationary electrons. If the scattering is to be produced by electrons, it must be due to the electrons in the ionized gas and these as we have seen have velocities much lower than those of the primaries. Let us therefore consider the scattering of a beam of electrons when it enters a cloud of stationary electrons. If we assume that the collisions follow the laws of elastic spheres we find that an electron which

* *Note added Sept. 2, 1925.* In some recent experiments two straight tungsten filaments 1 cm long were mounted parallel to one another at a distance of about 1 mm, so that two electron beams could be obtained that were practically coincident. In this case the primary electron temperature depended only on the *sum* of the electron emissions from the two cathodes, showing that the scattering did not occur within the cathode sheath but resulted from some effect taking place throughout the space travered by the primary electrons.

has made one collision with a stationary electron has on the average lost one half its momentum in the forward direction and has given half its energy to the other electron. Thus, if we have a beam of electrons which are moving with a homogeneous velocity corresponding to a voltage V_0 and we let this beam encounter a cloud of stationary electrons so that each electron in the beam makes one collision with an electron, we find that the translational velocity of the beam is reduced to a value corresponding to $\frac{1}{4}V_0$. An observer, moving along with this retarded beam, will see that the electrons in the beam are now moving in random directions with velocities corresponding to the energy $\frac{1}{4}V_0$. The effect of a single collision for each electron thus causes a decrease in the longitudinal energy of the beam of ΔE_l and an increase in the *random* energy ΔE_r given by

$$-\Delta E_l = \tfrac{3}{4}V_0 e \tag{11}$$

$$\Delta E_r = \tfrac{1}{4}V_0 e \tag{12}$$

the ratio being

$$-\Delta E_l/\Delta E_r = 3 \tag{13}$$

The electrons in the retarded beam cannot, however, in this case get a Maxwellian velocity distribution. There is no mechanism by which an electron can acquire velocities exceeding those in the original beam. If the number of electrons in the cloud is so small that the average decrease in the longitudinal energy is say 5 percent (about the average observed in our experiments) then 93.3 percent of the electrons have made no collisions at all and must retain all their original translational energy while 6.7 percent have lost 3/4 of their original energy. This would give a velocity distribution having no resemblance to a Maxwellian distribution. Thus we must conclude that the observed scattering cannot be due to the direct action of electrons upon those in the beam.

Scattering by clouds of entities of very small mass. If the particles in the cloud have masses m_p negligibly small in comparison to those of electrons, these difficulties disappear. In this case the fractional decrease in the translational velocity v_l of an electron in the beam is[8]

$$-\frac{\Delta v_l}{v_0} = \frac{4}{3}\frac{m_p}{m}n \tag{14}$$

where n is the number of collisions, and v_0 is the original velocity of the electrons in the beam. The decrease in longitudinal energy is thus

$$-\Delta E_l = \tfrac{4}{3}m_p v_0^2 n = \tfrac{8}{3}(m_p/m)nV_0 e\,. \tag{15}$$

[8] See Eq. (789) in Jeans' Dynamical Theory of Gases, 2nd Edition, p. 282. Cambridge, 1916.

A particle of velocity v_p colliding with an electron in the beam delivers its whole momentum $m_p v_p$ to the electron and the energy E thus acquired by the electron is

$$E = (m_p/m)E_p \tag{16}$$

where E_p is the kinetic energy of the particle. Since the energy of the particles which *strike* the electron is $2kT_p$ we have for the average random energy after n collisions

$$\Delta E_r = 2nkT_p(m_p/m)\,. \tag{17}$$

This average energy corresponds to $\frac{3}{2}kT$ so that the temperature of the primary electrons after n collisions is

$$T = \tfrac{4}{3}nT_p(m_p/m). \tag{18}$$

By comparing Eqs. (15) and (17) we find for the ratio of the decrease in longitudinal energy to the increase in random energy

$$\frac{-\Delta E_l}{\Delta E_r} = \tfrac{4}{3}\,\frac{V_0 e}{kT_p}\,. \tag{19}$$

For convenience we may express T_p in terms of the equivalent voltage V_p defined by

$$V_p e = kT_p \tag{20}$$

so that (19) becomes

$$\frac{-\Delta E_l}{\Delta E_r} = \tfrac{4}{3}\,\frac{V_0}{V_p} \tag{21}$$

Scattering by quanta. The momentum of a quantum of energy $h\nu$ is $h\nu/c$. If this quantum acts on an electron it may deliver to the electron any momentum between 0 and $2h\nu/c$ according to the direction taken by the scattered quantum. If the quanta are scattered with equal probability in all directions, as if by elastic spheres, the average momentum transferred may be taken to be $h\nu/c$. The average energy delivered to the electron by n collisions is

$$E_r = \tfrac{2}{3}\,n(h\nu)^2/mc^2. \tag{22}$$

Thus after n collisions with quanta the electron temperature is

$$T = (4/9)\,n(h\nu)^2/kmc^2\,. \tag{23}$$

We may conveniently express the energy of the quanta $h\nu$ in terms of the equivalent voltage V_q according to the relation

$$h\nu = V_q e\,. \tag{24}$$

Introducing the numerical values of k, m, c and e and expressing V_q in volts, Eq. (23) thus reduces to

$$T=0.0102nV_q^2. \tag{25}$$

Thus, for example, with quanta of a frequency corresponding to 50 volts, the temperature of the electrons increases by 25° for each collision with quanta.

The fractional decrease in drift velocity of the electrons after n collisions with quanta is

$$-\Delta v_l/v_0=4nh\nu/3mc^2=2.62\times10^{-6}nV_q \tag{26}$$

and the decrease in longitudinal energy is thus

$$-\Delta E_l=4v_0^2nh\nu/3c^2=\tfrac{4}{3}(v_0/c)^2nV_qe. \tag{27}$$

Comparing this with (22) we find

$$-\Delta E_l/\Delta E_r=4V_0/V_q. \tag{28}$$

Relation between the retardation and the scattering. Let us compare these calculated values of $\Delta E_l/\Delta E_r$ with the results of the experiments. In the experiment for which data were given in Fig. 1 the retardation corresponded to 2.8 volts and the electron temperature, due to scattering, was 1420°. The average energy in random direction E_r corresponds to $\frac{3}{2}kT$, so to express E_r in volts we divide the temperature by 2/3 of 11600, or 7730. Thus we find $-\Delta E_l/\Delta E_r=15.3$; i.e., the loss of energy by retardation is 15.3 times as great as the thermal energy of the scattered electrons.

Comparing this result with Eq. (28), we find $V_0/V_q=3.8$, and therefore $V_q=13$ volts since $V_0=50$ volts. Thus, quanta of a frequency corresponding to 13 volts would produce the ratio of retardation to scattering which was found by the experiments.

Rather variable results are obtained from other experiments. For example, the last column of Table I gives values of $-\Delta E_l/\Delta E_r$ ranging from 3.8 to 77, which would correspond to quanta having frequencies corresponding to voltages V_q from 53 down to 2.7. These values are all of reasonable order of magnitude, since radiation of such frequencies may well be present in gases excited by electrons of 50 volts energy.

If we assume that the scattering occurs according to the laws of the kinetic theory, by Eq. (21), the voltages corresponding to the energies of the particles will be 1/3 of those just found for V_q. These values also seem possible, although less probable, and we therefore cannot decide between the two theories from these data. Since, however, no entities

other than quanta are known having masses less than those of electrons, we will confine our attention at present to scattering by radiation.

Magnitude of Compton effect. According to the classical electromagnetic theory[9] the scattering coefficient of light by free electrons is

$$\alpha = 6\pi a^2 n_e, \tag{29}$$

where α is the fraction of energy scattered per unit length of path through a region occupied by n_e electrons per unit volume and a is the radius of the electron by Lorentz's theory ($a = 1.88 \times 10^{-13}$ cm). Thus we find

$$\alpha = 6.7 \times 10^{-25} n_e \text{ per cm}. \tag{30}$$

According to the correspondence principle, we should expect approximately this amount of scattering even if the scattering takes place by quanta. For metallic aluminum $n_e = 8 \times 10^{23}$ electrons per cm^3, so we obtain $\alpha = 0.53$ per cm, which gives a scattering of the order of magnitude found for the Compton effect.[10] For a mercury arc n_e is of the order of 10^{10} electrons per cm^3, so that α should be about 10^{-14}. This is in accord with the fact[11] that no Tyndall cone is observed when a strong beam of sunlight is focussed by a large lens into a nearly non-luminous 2-ampere arc in argon at a few millimeters pressure.

With a primary electron current of 10 m-amp. and 50 volts, the total energy escaping from the disk-shaped electron beam is about 0.02 watt per cm^2, or about 5×10^{15} quanta ($V_q = 25$ volts) per cm^2 per second. With a scattering coefficient of only 10^{-14} there would be 50 quanta scattered per cm^3 per second. To give the observed electron temperatures of 1420° each electron would have to make (according to Eq. 25) 230 collisions with quanta. Since there are 6×10^{16} electrons per second in the primary beam, the number of collisions per second would need to be 1.5×10^{19} or about 3×10^{17} per cm^3 per second, instead of the 50 collisions calculated above.

Thus, the observed scattering is about 10^{16} times greater than that to be expected from a normal Compton effect.

This difficulty seems to be very similar to that met with in connection with the theory of chemical reaction velocity[12] where it is found that a chemical molecule must become activated millions of times more frequently than it collides with other molecules. Yet the energy that it can

[9] Leigh Page, Astrophysical Jour. **52**, 67 (1920).

[10] Since the frequencies of x-rays are sufficient to remove most of the electrons in aluminium, we may consider the electrons as free electrons in regard to the scattering of this kind of radiation.

[11] According to rough experiments in this laboratory.

[12] Langmuir, Jour. Amer. Chem. Soc. **42**, 2190 (1920).

receive by radiation, according to the usual radiation laws, is millions of times too small to cause this activation.[13]

Scattering by the joint action of radiation and excited atoms. Because of the small magnitude of the Compton effect we must conclude that the scattering of electrons is not due to any direct interaction between them and radiation. It may well be, however, that the effect is due to an *interaction between radiation, excited atoms and electrons.*

Resonance radiation is enormously strongly scattered by excited atoms, practically all the radiation coming within a distance of about one-half wave-length from an excited atom being scattered, whereas the radiation scattered by an electron is only 6 times that falling on an area equal to the cross-section of the electron. For radiation corresponding to 25 volts the wave-length is 490A. The radiation scattered by an excited atom of a 25 volt energy level is thus about 10^{14} times greater than that scattered by an electron. This is about the order of magnitude of the ratio (10^{16}) of the observed scattering to that calculated for a normal Compton effect. If resonance radiation is trapped within the region traversed by the primary electrons, the ratio 10^{16} would be reduced, so that it might well be brought down to the value 10^{14} corresponding to the radiation scattered by excited atoms.

When a quantum of resonance radiation is scattered by an atom or excited atom the direction of the quantum is changed and the difference of momentum is available to deliver an impulse to some particle. Although we would expect in general that the momentum would be delivered to the atom or excited atom, it may well be that if an electron is close enough, the momentum may be delivered to the electron. In some such way as this we may suppose that the electrons can receive momenta whose magnitude is in accord with Compton's theory, although the probability that an electron may receive this momentum is 10^{14} times greater than according to the normal Compton effect.

Consider the excitation of a mercury atom by a quantum of resonance radiation (λ2537). The difference in the angular momentum of the atom before and after excitation must be a multiple of $h/2\pi$. Before the encounter, the two-body system, consisting of atom and quantum, will also contain an angular momentum equal to the product of the momentum $h\nu/c$ of the quantum, by the distance between the center of the atom and the path of the quantum. This angular momentum in general will not be a multiple of $h/2\pi$. After the collision we have a one-body system having a fixed angular momentum. Thus, it would seem that a

[13] See also a recent paper by R. C. Tolman, Jour. Amer. Chem. Soc. **47**, 1524 (1925).
[14] Barkhausen and Kurz, Phys. Zeits. **21**, 1 (1920).

mercury atom can be excited by a quantum only if a third body is present which can take up the residual angular momentum. An electron within a distance comparable to a wave-length may serve as such a third body and may thus increase the ease with which excited atoms are formed. Perhaps without such third bodies, resonance radiation cannot even be scattered, although it is not necessary to draw this conclusion, since scattering involves a two-body problem both before and after the scattering. Experiments to determine whether the scattering coefficient of resonance radiation is dependent on the presence of free electrons are in progress by Mr. Whitten in this laboratory. An attempt will also be made to determine whether low velocity electrons in mercury vapor or sodium vapor are scattered when resonance radiation is allowed to act on the vapor.

The loss of energy by retardation of a beam of primary electrons is always much greater than the energy that appears as thermal energy of the scattered electrons. A beam of primary electrons may thus deliver energy directly to the radiation, or to excited atoms, by the reverse of the process that causes scattering of the electrons. Thus the average frequency of the radiation in the primary beam probably increases as the current density of the beam is raised. This may be the reason that the primary electron temperature increases with the square or even with a higher power of the current density.

As an alternative hypothesis to account for the large amount of electron scattering, we may assume that the presence of an electron within a distance comparable to a wave-length from an excited atom, greatly increases the probability that the excited atom will emit a quantum of radiation. Thus, the average intensity of radiation near the electron would be much greater than that in the space as a whole and the magnitude of the Compton effect would thereby be increased. The momentum delivered to the electron in this case may, however, be very much greater than that due to a Compton effect. Of course, if an electron increases the probability of emission of radiation by an excited atom it must also increase the probability of the absorption of a quantum by an atom according to the reverse process. If scattering of resonance radiation is due to quantum jumps then, the scattering should be increased by the presence of electrons.

IV. Explanation of Maxwellian Distribution of Ultimate Electrons

We have seen that the primary electrons from a cathode at -50 or -80 volts are scattered mainly by some direct effect of the primary

electrons and not by the action of the ionization or excitation caused by the secondary or the ultimate electrons. In the positive column of an arc primary and secondary electrons are absent. It might seem, therefore, that the mechanism by which the electrons in an arc acquire their Maxwellian distribution must be different from that which causes the scattering of primary electrons. It seems more probable, however, that the mechanism is essentially similar, the difference being merely one of degree.

For example, in an arc in mercury vapor at 5 bars pressure the temperature of the ultimate electrons is about 20,000°, corresponding to an average energy ($\frac{3}{2}kT$) of 2.6 volts. According to Eq. (25) the corresponding radiation (λ4700) would increase the temperature of electrons by only 0.08° for each quantum scattered, whereas 50 volt radiation which might exist in the primary beam could raise the temperature by 25° per collision.

In the case of the ultimate electrons in an arc it seems probable that there is a kind of thermal equilibrium between the electrons and the radiation and excited atoms. That is, the electrons lose as much energy to the radiation on the average, as they gain from it. Thus there is probably a definite relation between the temperature of the ultimate electrons and the frequency of the ultraviolet radiation or the average energy levels of the excited atoms.

The effective electron free-path determined from the mobility of electrons in an arc is not the average distance the electron moves before being acted on by a quantum, but is the distance it must move before losing most of its momentum in a given direction. By Eq. (26) we see that an electron will lose about half its forward momentum when it has made 190,000 collisions with quanta of a frequency corresponding to 2.6 volts. The experiments have given an effective free path of about 3 cm at one bar so the distance between successive interactions with quanta would average 1.5×10^{-5} cm.

It will be understood that the foregoing theoretical considerations are purely tentative. The fundamental cause of electron scattering can be established only after further experimental studies of the laws governing it.

V. Scattered Electrons in High Vacuum Tubes.

One of the most striking characteristics of electron scattering is the ability of some electrons to pass to an electrode which is more negatively charged than the cathode from which the electrons originate. A similar phenomenon is observed in vacuum tubes having apparently the highest

vacuum if the anode consists of one or more wires of small size at high positive potential while a surrounding cylindrical electrode is negatively charged with respect to the cathode. A current of electrons flows to this cylinder. This effect, discovered by Barkhausen and Kurz[14] was explained by them as being due to electrical oscillations of electrons in the evacuated space. These oscillations were actually detected by Barkhausen and Kurz. Gill and Morell[15] have outlined a theory which suggests a cause of the oscillations.

Experiments in this laboratory, however, have shown that although oscillations frequently exist in such a tube they do not seem to be the sole cause of the currents to the negative cylinder. For example, in some experiments the logarithm of the current to the cylinder varied linearly with voltage on the cylinder suggesting a Maxwellian distribution of the high speed electrons in the space. The temperature of these electrons was found to be proportional to the potential on the anode. With cylinder potentials close to those of the cathode electrical oscillations were observed, but when the cylinder was made more strongly negative the oscillations stopped abruptly and completely as far as could be determined, and simultaneously the current to the negative cylinder *increased* several fold.

Similar effects are observed in a magnetron having end plates charged negatively with respect to the cathode. A longitudinal magnetic field tends to prevent electrons from reaching the cylindrical anode and the negative potentials on the end plates tend to prevent their escaping at the ends of the cylinder. Under these conditions, small currents of electrons do flow to the cylinder in spite of the magnetic field and flow to the end plates even if these are 20 to 50 volts negative with respect to the cathode. Exact oscillations can very rarely be detected. These experiments have been repeated by Mr. C. G. Found with the very best vacuum conditions using an anode of deposited magnesium on the glass wall and immersing the whole apparatus in liquid air, but the currents to the negative electrodes were not decreased.

It will be noted that these effects might be explained if the trapped electrons in the Barkhausen-Kurz tube or in the magnetron were scattered so as to obtain a Maxwellian distribution. However, it is hard to see how this distribution can be brought about with so few excited atoms and so little radiation as must be present in these tubes.

[15] Gill and Morell, Phil. Mag. **44**, 161 (1922).

VI. Oscillations as a Possible Cause of Scattering in Ionized Gases

Since oscillations occur so often in tubes of this character and have been suggested as a cause of the currents to negative electrodes, it has been felt throughout the experiments on the scattering of electrons in ionized gases, that it is important to determine whether oscillations are present. For this reason we have frequently used radio detectors capable of detecting oscillations of 0.5 meter wave-length and have introduced small capacities and inductances in various parts of the circuits to see if any of the currents to collectors could be modified in this way. In none of the experiments on electron scattering in low pressure gases using hot cathodes have oscillations been observed. In some experiments with mercury arcs oscillations occurred at first until high resistances or choke coils were used in the anode circuits. The effects produced by the oscillations were not at all like those characteristic of electron scattering.

Research Laboratory,
General Electric Co.,
Schenectady, New York.
July 16, 1925.

RELATIVE PRODUCTION OF NEGATIVE AND POSITIVE IONS BY ELECTRON COLLISIONS[1]

By F. L. Mohler

Abstract

In the tube used, either positive or negative ions produced by an axial beam of electrons accelerated from a filament by a voltage V, were collected on a concentric cylindrical electrode D by maintaining it at a potential slightly lower or higher than that of the beam, the primary electrons being prevented from reaching D by means of a solenoidal magnetic field of 100 gauss parallel to the axis. While saturation was not always reached, the relative values of the positive and negative ion currents are significant. Contrary to the ordinary theory, the polar compounds *mercuric chloride* and *hydrogen chloride* gave results quite similar to those for the elements *mercury and iodine*. With electron currents of the order of 10^{-6} amp. and pressures of about .001 mm, the negative ion current is in all cases small compared with the positive ion current above the ionization potential. With larger currents the negative current increases sharply at the ionization potential and the ratio to positive current is greater. For vapors other than mercury there are some negative ions produced at all voltages, the negative ion currents each having a maximum at zero and increasing again at certain critical potentials, the voltages being 4 for $HgCl_2$, 6.5 for HCl and 2.4, 4.6, 8.4 for I_2. As far as is known, these potentials are equal to *potentials of inelastic collision*. These experiments give no support to the theory that electron collisions dissociate polar molecules into positive and negative ions. In agreement with the results of the magnetic analysis of positive ions, they indicate that the primary effect of an electron impact is the production of a positive molecule ion. The negative ion curves obtained can be explained by the hypothesis that only slow moving electrons attach themselves to molecules to form ions, but the absence of low voltage negative ions in the case of Hg is not understood.

IT is generally assumed that negative ions are produced by electron collision in two different ways, by an electron attaching itself to a neutral molecule, and by an electron collision splitting the molecule into a positive and negative ion.

Measurements[2] of electron mobility indicate that some normal molecules readily form ions by attachment of electrons, notably chlorine and oxygen, while hydrogen, nitrogen and the rare gases show complete absence of negative ion formation. On the other hand electromagnetic resolution of the ions formed in an electric discharge shows the presence

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Loeb, Phil. Mag. **43**, pp. 229-236 (1922).

of negative ions in other gases including those just excepted.[3] The experiments are not contradictory, however, for Franck and Grotrian[4] have pointed out that atoms or molecules in excited states will have properties entirely different from normal molecules and in some states may well have a strong electron affinity. Mobility measurements are made under conditions insuring almost complete absence of excited molecules while quite the contrary is true in the experiments involving electromagnetic analysis of the ions.

The assumption that electron collisions may dissociate molecules into positive and negative ions is based on the numerical agreement between the computed work required to so dissociate polar molecules and the observed ionization potentials. The hydrogen halides offer the only instance where the data compared are entirely satisfactory and the agreement in these instances is remarkably good. Table I gives some results. It has, however, been questioned whether these data give conclusive proof as to the nature of the ionization process.[5]

TABLE I

Ionization of hydrogen halides.[6]

Halide	Work to separate ions	Observed ionization potentials (Knipping)	(Mackay)	(Foote and Mohler)
H Cl	13.7	13.7	13.8	14.0
H Br	13.1	13.3	13.2	
H I	12.7	12.7	12.8	

The methods of electromagnetic analysis have recently been applied to the low voltage thermionic discharge and important information is being obtained on the minimum potentials required to produce positive ions of known e/m ratio.[7] An inherent limitation of the method makes it difficult, however, to measure the formation of negative ions as a function of the voltage. In the method here described use is made of a magnetic field merely to separate the heavy ions from the electrons.

EXPERIMENTAL METHOD

Fig. 1 indicates diagramatically the arrangement of electrodes in the electron tube used. The filament A and the diaphrams B produce a beam of electrons which passes along the axis of the cylindrical electrode D to the wire gauze electrode C and plate C'. A helix around the entire

[3] J. J. Thompson, "Rays of Positive Electricity" p. 70 et seq.; Smyth, Proc. Roy. Soc. **104A,** 121 (1923).

[4] Franck and Grotrian, Zeits. f. Phys. **4,** 89-90 (1921).

[5] Mackay, Phys. Rev. **24,** 319 (1924).

[6] Compton and Mohler, "Critical Potentials and Their Interpretation," Bull. Nat. Res. Coun. No. 9, p. 112 (1924).

[7] Smyth, J. Frank. Inst. **198,** 795-811 (1924); Phys. Rev. **25,** 452 (1925).

tube gives a magnetic field H of about 100 gauss parallel to the axis and to the electron beam. For ion measurements potentials are applied as indicated in the figure. The electron speed is determined by the variable potential difference V and V_2 is a relatively small potential, usually ± 1 volt, which draws the ions to the receiving electrode. The electrons move in a nearly equipotential region and in the absence of a magnetic field any gas in the tube will tend to scatter them to the side electrode. The current from scattering was found to be large compared with the ion current, a result in accord with published data[8] on scattering and ionization. In argon at 25 volts the probability of scattering is 10 times that of ionization and at 17 volts about 100 times as great. The function of the magnetic field is to prevent this scattered current reaching the side electrode.

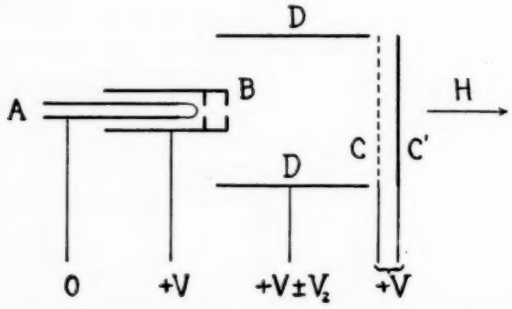

Fig. 1. Arrangement of electrodes and method of applying potentials for measuring either positive or negative ions. The arrow H indicates the direction of the magnetic field.

Electrons[9] having a velocity corresponding to a potential of V volts moving in an equipotential space at right angles to a magnetic field H will describe circles of radius.

$$R = 3.4\sqrt{V}/H.$$

In the form of tube here used an electron moving along the axis is unaffected by the magnetic field but if it is deflected by a single molecular collision through an angle θ it will move in a helix of radius

$$R = (3.4\sqrt{V}/H)\sin\theta.$$

This helix is tangent to the axis so that the electron departs from the axis a maximum distance $2R$. Electrons scattered at 90° reach a distance $6.8\sqrt{V}/H$ from the axis. Ten-volt electrons in a field of 100 gauss will after a single scattering move on helices within .2 cm of the axis.

[8] A. L. Hughes, "Collisions between electrons and molecules," Washington Univ. Studies **11**, 117-152 (1924).

[9] Hull, Phys. Rev. **18**, 34 (1921), gives equations for the motion of electrons in superposed electric and magnetic fields for various electrode shapes. This paper and one by Richardson and Chaudhuri, Phil. Mag. **45**, 337-52 (1923), include some experimental results on the effect of a trace of gas on the motions.

The radius of the cylinder D was about 1.5 cm. An ion of mass 35 relative to hydrogen and with a velocity corresponding to one volt will move on a path with a radius of curvature of about 9 cm. It follows that with the conditions here used the scattering of electrons to the side electrode can be prevented without seriously affecting the motion of the heavy ions.

The magnetic field introduces one complication. Without the field the diaphrams B limit the current to electrons which move along the axis. In the presence of the field electrons move on helices tangent to the axis so that electrons starting at angles of θ between 0° and 90° may be able to pass through the diaphrams. An electron which starts at an angle θ and velocity v, moves along the axis with a speed $v \cos \theta$ and traverses a path of length $1/\cos \theta$ in unit distance along the axis. The stopping potential at a surface normal to the axis will be $V \cos^2 \theta$. Curves of retarding potential between C and C' versus current reaching C' indicate that actually many electrons had large values of θ. The form of the electrodes precludes detailed mathematical analysis but it seems probable that the average value of θ and hence the average length of electron path will vary with the voltage so that quantitative conclusions concerning the production of ions at different voltages cannot be drawn.

To avoid multiple electron collisions and other complicating effects, these experiments were limited to low pressures (less than .01 mm) and small electron currents (between 10^{-5} and 10^{-6} ampere). The positive ion currents were of the order of one percent of the electron current. The construction of the electron tubes was modified in various details during the course of the work but with no important effects on the results.

The tubes showed the following characteristics. The curve of electron current to CC' versus V rose rapidly from near the origin in the first few volts and reached a nearly constant value above 6 or 8 volts. The curve of positive ion current to D as a function of V_2 rose sharply from a point between +.55 and zero volts and reached saturation at a negative potential of 2 volts or more. Only at the lowest pressures and currents did the ion current at $V_2 = -1$ approximate the total production of ions. A 50 percent change of the magnetic field in either direction had little effect on the ion current.

Vapor pressures of iodine and mercury were controlled by the temperature of a side tube in which they were contained while the pressure of $HgCl_2$ was determined by the temperature of the main tube. HCl was streamed through a fine capillary tube from a reservoir containing gas at pressures between 76 and 10 cm.

Experimental Results

Figs. 2 to 4 show currents to D as a function of the voltage V applied to the electron current, except that curves marked SP give electron currents reaching C' against a retarding potential between C and C', the potential V being constant. Positive ion currents to D at $V_2 = -1$ volt are indicated by P, negative ion currents with D at $V_2 = +1$ volt, by N. The current per unit electron current would give a curve of different shape in the first few volts. Table II gives data on experimental conditions for these curves. Initial potential corrections were made on the basis of published measurements of ionization potentials. Table III lists the reference values as well as observed values of other potentials relative to these.

Table II

Currents and pressures* for curves of Figs. 2, 3 and 4.*

Vapor	Curve number	Pressure (mm)	Electron current (10^{-6} amp.)	Pos. ion current (10^{-8} amp.)	Neg. ion current (10^{-8} amp.)	Pot. V for current meas.
Hg	PII, NII	.001	.95	2.3	.1	18 volts
	PI, NI	.002	.92	3.7	.6	18
$HgCl_2$	PI, NI	< .003	2.0	3.7	.3	16
	NII	< .003	6.0	....	3.4	16
H Cl	PIV, NIV	.0005	3.2	1.1	.07	18
	PIII, NIII	.001	2.9	2.3	.34	18
	PII, NII, NI	.001	7.5	16	5.5	18
	NV	.002	4.3	(24)	7.7	18
I_2	PIII, NIII	.002?	12.6	2.8	.38	15
	PI, NI	.01	6.9	22	9.5	15
	NII	.01	(3.5)	(120)	....	15

* Values in parentheses are from data not plotted. Pressures are in general not accurate.

Table III

Critical potentials for production of ions.

Vapor	For positive ions	For negative ions
Hg	10.4*	10.4
$HgCl_2$	12.1*	12.1
		4.
HCl	13.8*	13.8
	23.5	6.5
I_2	10.0*	10.0
		2.4
		4.6
		8.4

* These are published values for the first ionization potential (see ref. 5).

The middle section of Fig. 2 gives three curves obtained with mercury vapor at low pressure and with a small electron current. The negative current is practically negligible as compared with the positive. The upper curves of this figure were obtained with the same electron current but higher pressure and show that the negative ion current starts sharply at the ionization potential. With larger currents and pressures the

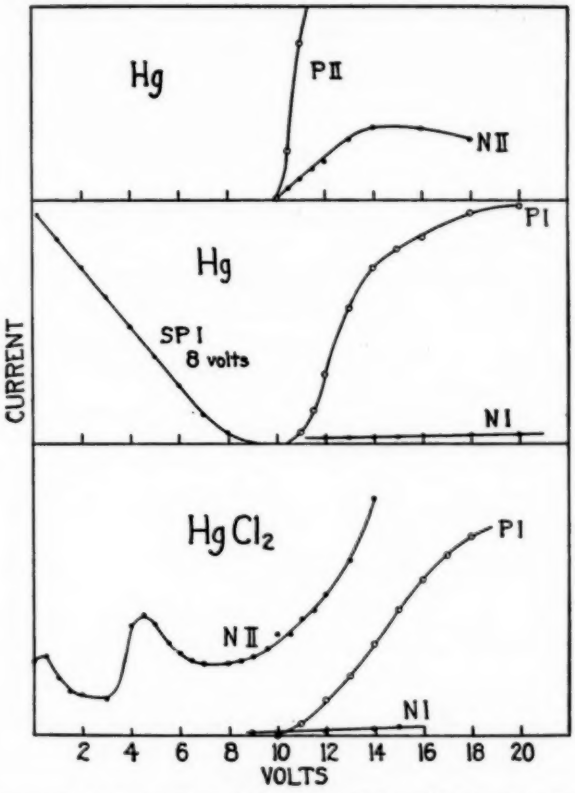

Fig. 2. Ion currents as a function of the potential applied to the electron current. Positive ion curves indicated by *P*, negative by *N*. Curve *SP* shows current against retarding field between *C* and *C'*.

negative ion currents became nearly equal to the positive but under these conditions the ion currents were far from saturated so that there is no reason to believe that the production of ions was equal.

The lower part of Fig. 2 shows ion currents in $HgCl_2$ at 60°C (saturation pressure .003 mm). The chloride was partially dissociated upon evaporation as evidenced by the formation of a film of the less volatile mercurous chloride. Curves PI and NI obtained with low electron current indicate that here too the production of negative ions is small compared with the

amount of positive ions above the ionization potential. However, some negative ions were in this case present at all voltages; curve NII shows on a much larger scale the low voltage portion of a negative ion curve. There is a maximum near zero volts and an increase at an applied potential of about 3 volts (corrected value 4 volts).

Fig. 3 gives current voltage curves in hydrogen chloride. This gas is of particular interest in view of the theoretical considerations mentioned above. The liquid air traps used for freezing out mercury prevented

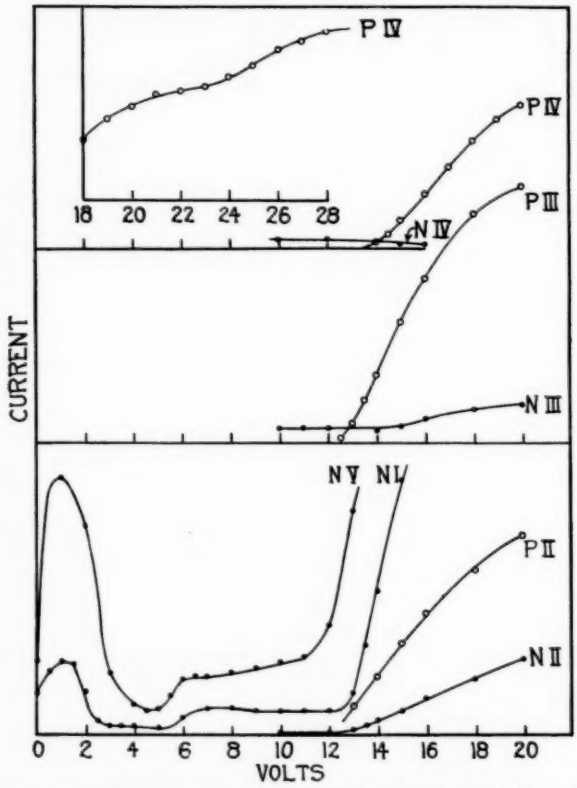

Fig. 3. Positive and negative ion currents in HCl as a function of the applied potential.

the measurement of the pressure under working conditions so that values given in Table II are only rough estimates. Curves PIV, NIV, PIII and NIII, obtained with low pressure and small currents, are, contrary to theory, quite similar to the results obtained in mercury vapor under similar conditions. Above the ionization potential the positive ion current is predominant. The small negative current is, however, measurable at all voltages. The curves in the lower part of the figure were obtained with larger currents and pressures and are similar in general form to those

obtained in $HgCl_2$ under like conditions. The ion current *per unit electron current* if plotted would drop sharply from zero volts. There is an increase near 6.5 volts (a large correction has to be added) and another at the first ionization potential. Positive ion currents show a well defined increase at 23.5 volts.

Fig. 4 gives curves obtained with iodine vapor. The upper curves, with the vapor at low pressure, again show the positive ion production pre-

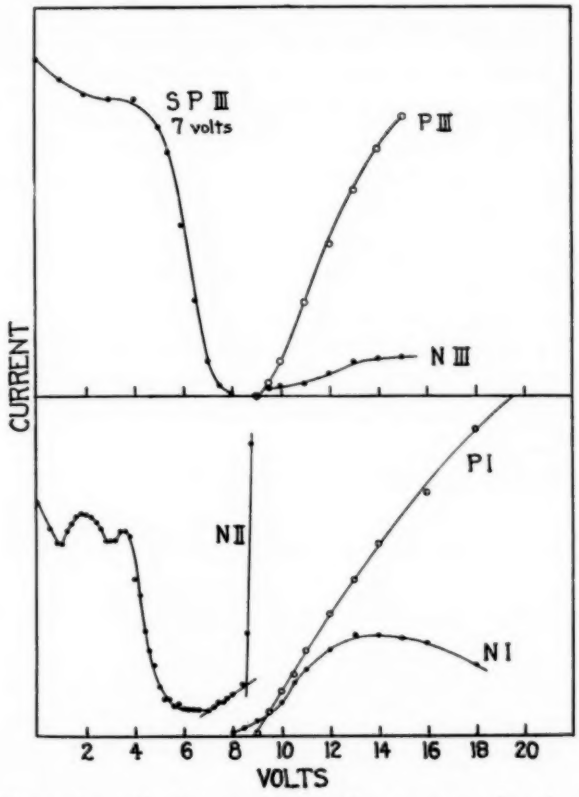

Fig. 4. Positive and negative ion currents in iodine vapor as a function of the applied potential.

dominant. The lower curves taken with much higher pressure show the general features of negative ion curves in the other polyatomic vapors but the critical potentials are in the case of NII exceptionally sharp.

Interpretation of Results

The ion currents above the ionization potential showed the same characteristics in all the gases studied. With low pressures and small electron currents the negative ion currents were negligible compared

with the positive. Increasing the pressure or the electron current made the negative ion current relatively larger and it increased sharply at the ionization potential. The increase with electron current was at first more rapid than the first power of the current (pressure and voltage being constant) while the positive current increase was less than that of the electron current because of departure from saturation.

If polar molecules were ionized into positive and negative ions the results with mercury and iodine should be in marked contrast to those with mercuric chloride and hydrogen chloride. With the latter gases the production of positive and negative ions should be exactly equal. The measured currents would not always be equal as the heavier ions would depart more from saturation, but the two currents would approach equality as the pressure and current were reduced. The observed phenomena are quite different and seem to show conclusively that ionization by dissociation is not the primary effect of the electron collision. The negative ion formation above the ionization potential seems to be a secondary effect depending possibly on the amount of excitation as well as on the current. It is not clear why this secondary effect should start exactly at the ionization potential. The theory of Franck and Grotrian[4] indicates that it would start at some lower critical potential.

All the polyatomic vapors, in contrast to mercury, showed a negative ion current at low voltage. The current dropped rapidly from a maximum at zero volts and increased again at well defined critical potentials. The low voltage current was roughly proportional to the electron current in contrast to the condition above the ionization potential. The critical potentials for iodine were determined with fair precision as 2.4, 4.6, 8.4 and 10.0 volts. Iodine gives potentials of inelastic collision at multiples of 2.3 volts and ionization at 10 volts while there is known to be another excitation stage slightly below 10. These potentials apparently agree with the critical points on the ion curve and suggest a simple hypothesis to account for the form of the curve. Assume that only very slow electrons attach themselves to molecules to form negative ions. Then ions will be formed not only near zero volts but also immediately above potentials of inelastic collision, the function of the collision being merely to reduce the speed of the electron. As the potential is increased beyond the critical value electrons will not lose all their speed and the ion production will again decrease. Conditions are different above the ionization potential for there is reason to believe that slow electrons are produced by ionization even though the voltage is far in excess of the critical potential. Potentials of inelastic collision are not known for HCl and $HgCl_2$.

Loeb[10] has shown from analysis of mobility measurements that the probability of electron attachments can be expressed by an equation in which the probability is independent of the electron speed. However, the equation involves the assumption that electron free paths are independent of the speed, which is not strictly true especially at very low speeds. He concludes that the probability of attachment may decrease as the speed increases but that the existence of a "critical potential" for the production of negative ions is excluded. Our results are not inconsistent with this view but many more data are needed before conclusions of any generality can be drawn.

As concerns the process of ionization of polar molecules, while our conclusions are opposed to a commonly accepted theory, they find support in experimental results on positive ray analysis, which show that in general both molecule ions and atom ions are formed in a discharge. J. J. Thompson[11] concludes from data on a great many compounds under different conditions that, with either polar or non-polar molecules, the immediate effect of a collision of a high speed electron is the production of a molecule ion without dissociation. Results with low speed electrons are relatively few and are less conclusive on this point.

Dempster[12] studied ions formed in a thermionic discharge through hydrogen at potentials as low as 90 volts and found that H_2^+ was the primary product of electron collision. Recently Smyth[13] has carried out similar experiments with voltages as low as the ionization potential.[13] Except at very low pressures H^+ and H_3^+ were found, but he gives evidence that they are produced by collisions of H_2^+ with other molecules.

A recent paper[14] on ions formed at low voltage in $HgCl_2$ and HgI_2 is in apparent contradiction to the present results. Cl^- and I^- were found above the first ionization potential, which led them to conclude that the ionization process was of the type $HgCl_2 \rightarrow HgCl^+$ and Cl^-. Positive rays from the chloride discharge contained $HgCl_2^+$, $HgCl^+$, Hg^+ and Hg^{++}. The results are not actually inconsistent with ours for relatively large electron currents are essential in experiments on positive ray analysis and our data show that except with very small currents the production of negative ions is large and increases at the ionization

[10] Loeb, J. Frank. Inst. **197,** 45-55 (1924).

[11] J. J. Thompson, "Rays of Positive Electricity," p. 88 *et seq.*

[12] Dempster, Phys. Rev. **8,** 651-662 (1916).

[13] Smyth, Phys. Rev. **25,** 452-468 (1925). These results indicate that previously published measurements with nitrogen and oxygen as well as hydrogen may have been misinterpreted.

[14] Kondratjeff and Semenoff, Zeits. f. Phys. **22,** 1-8 (1924).

potential. Thermal dissociation will account for the presence of atomic chlorine and iodine.

A preliminary note[15] on ions formed in HCl gives results which are admittedly inconclusive. At 30 volts HCl^+ (or Cl^+), Cl_2^+, H^+ and H_2^+ are found and with decreasing pressure the hydrogen ions become more prominent. The presence of H_2^+ indicates that there was molecular hydrogen in the tube and makes the results ambiguous as regards the process of ionization of HCl.

In view of the conclusion that electron collisions do not dissociate molecules in the process of ionization, the agreement shown in Table I between computed and observed ionization potentials is an unexplained coincidence. This work in no way disproves the theory on which the computations are based. The theory gives the work required to separate a positive and negative ion and experiments show that an electron collision is not effective in producing such a separation but simply removes an electron from the molecule. Strangely enough the binding energy of the electron in the molecule is nearly the same as the binding energy of the positive and negative ion in the ideal polar molecule.[16]

BUREAU OF STANDARDS,
June 11, 1925.

[15] Barton, abstract in Phys. Rev. **25**, 890 (1925).

[16] I have had the privilege of reading proof of a paper by Barker and Duffendack (Phys. Rev. **26**, 339, 1925) which includes spectroscopic observations indicating that in pure HCl there is no radiation in the range of the quartz spectrograph even at 120 volts. They also show that the thermionic discharge gives no dissociation comparable with the thermal dissociation produced by the hot filament. Their conclusions are quite consistent with those here deduced from an entirely different type of experiment.

ON THE NATURE OF THE IONS FROM HOT PLATINUM

By Henry A. Erikson

Abstract

The mobilities of the ions produced by hot platinum were obtained by driving the ions across a stream of air by means of an electric field. The currents at a down stream point were obtained at different values of the field. The current voltage curves for the ions from platinum were compared with curves obtained in a similar manner using ions produced in air by alpha rays. An initial and a final positive ion and one negative ion were found, the same as in the case of the air ions. The mobility values obtained for these ions are also the same as for the air ions. A discussion of the results leads to the conclusion that the negative and final positive ions from platinum are air ions. The initial positive ion may also be an air ion, but this is less certain.

IN an earlier paper[1] results were reported showing that the positive ion from hot platinum has at first a mobility which is the same as the mobility of the negative air ion and the initial[2] positive air ion and that within an interval of the order of 0.3 sec. it changes into an ion which has the same mobility as the final positive air ion. It was also found that if the ions are allowed to remain for a time in the air which has passed the platinum, they load up and form a gradation of larger positive ions.

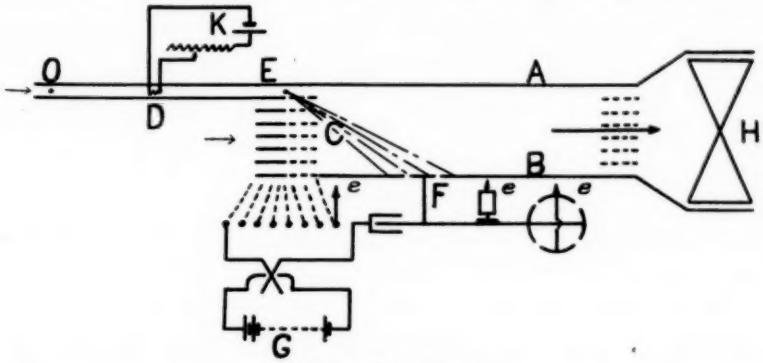

Fig. 1. Apparatus.

As these results were obtained by means of an apparatus which did not have a very high resolving power, it was thought desirable to repeat the work using an apparatus capable of more fully separating the two positive ions.

The method used may be briefly described as follows. By means of a fan H, air was drawn between the parallel plates A and B which were

[1] Erikson, Phys. Rev. **21**, p. 720 (1923).
[2] Erikson, Phys. Rev. **24**, p. 502 (1924).

3.5 cm apart and which were maintained at a difference of potential by means of the battery G. The platinum wire was placed at E, D, or O, and was heated by means of a current from the battery K. The ions formed at the platinum surface were carried with the air and when in the space between the plates A and B were drawn to A or B depending upon the sign of their charges. At plate B the current due to the ions coming to a narrow strip F was measured. These currents were obtained for different potentials between A and B. The currents are plotted as ordinates against the potentials as abscissas. By moving the platinum wire towards O, the age of the ions was increased. As the ion emission depends upon the length of time the wire has been heated, care was taken to keep the

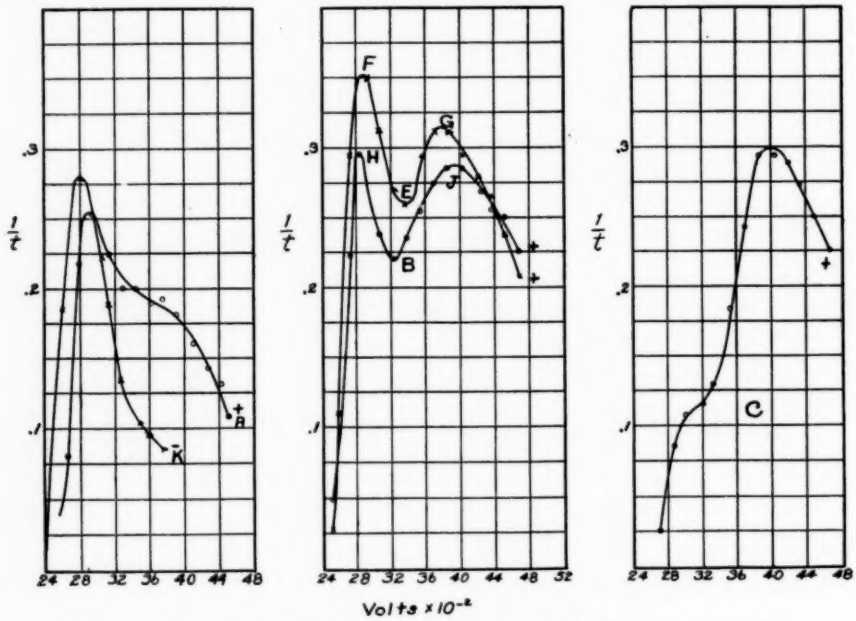

Fig. 2. Currents to strip F as a function of potential between A and B.

heating circuit open between readings. Continuous heating of the platinum during the hour or more required for a set of readings, causes a change in the ion emission which masks, in part, the effect sought for. In the case of the positive ion the platinum was kept at a deep red.

The Positive Ions

The results obtained, in the case of the positive ion, are shown in Fig. 2, where the ordinates represent the currents to the strip F in arbitrary units.

Curve HBJ was obtained with the platinum at D, Fig. 1, the median position. Curve FEG is for the positive ions produced in air by the alpha

rays from polonium placed at *D*, the conditions otherwise being identical, and is inserted for comparison. The maximum *F* of the air curve FEG is due to the initial positive air ion[2] and the maximum *G* is for the final positive air ion. These correspond respectively to mobilities of 1.87 and 1.36 cm/sec/volt/cm. It is thus seen that hot platinum gives rise to two positive ions which have the same mobilities as the initial and final positive air ions.

That the positive ion from hot platinum which gives rise to the maximum *H* in curve HBJ is an initial ion is shown by the series of curves A, B and C, Fig. 2. The three curves were obtained with the platinum at *E*, *D*, and *O*, Fig. 1, respectively. Comparison of these shows that this ion changes into the slower ion as it becomes older.

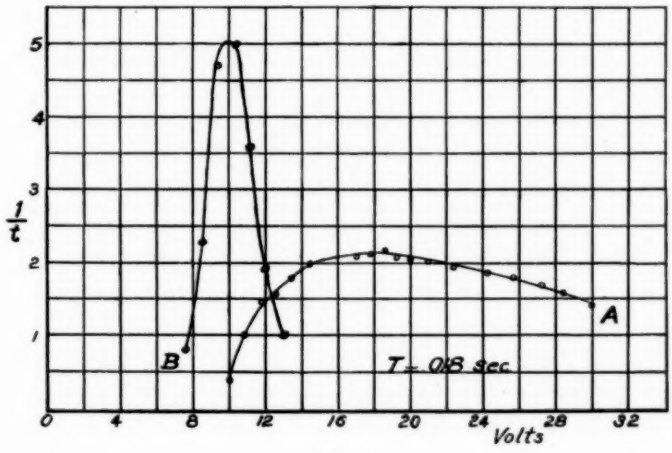

Fig. 3.

In Fig. 3, curve A shows the result when the platinum is placed at *O*, Fig. 1, the velocity of the air reduced, and the platinum raised to white incandescence. It is seen that a gradation of positive ions are obtained. In this case the ions are in an atmosphere of platinum dust for a considerable time and attach themselves to platinum particles of various sizes. Curve B, Fig. 3, is for the negative air ion and shows the position the initial positive ion from platinum would have if present. On account of this loading it is necessary if the pure initial effect is desired, to have the platinum at the lowest temperature which will give sufficient ions for measurement.

The Negative Ion

In Fig. 2, curve K is for the negative ion and was obtained by placing the platinum at *E*, Fig. 1, and heating it to incandescence. Indication of

only one ion was obtained. This ion, it is seen, has the same mobility as the initial positive ion from platinum and hence the same mobility as the negative air ion also.

Discussion as to the Nature of the Above Ions

The question as to the nature of the ions from hot platinum can not be completely answered from the standpoint of present experimental evidence. The writer believes, however, that the final of the two positive ions is formed when the initial positive ion attaches itself to a neutral air molecule. That this transition is possible is shown by satisfactory experimental evidence, not only in this but in earlier work on gas ions. It can with fair certainty be said also that the negative ion is an air molecule which has attached an electron since electrons are emitted from hot platinum and such attachments are known to be possible. That the initial positive ion is also an air ion can not be stated with equal certainty, although it is very probable that such is the case, as this ion is not formed continuously in a vacuum. It is difficult to make even a hypothetical statement as to the mechanism of its formation because the electron must pass from an air atom of higher electron affinity to one of lower. Langmuir and Kingdon[3] have shown that caesium atoms upon striking a clean tungsten surface lose valence electrons and leave the surface positively charged. The reason they give for this is that the electron affinity of tungsten is 4.53 volts whereas the electron affinity of caesium is only 3.88 volts and this reason seems entirely valid. In the case in question it is necessary for the electron to pass in the opposite direction. There may, however, be other determining factors. In the case of platinum in air at normal pressure it is one collision in about 10^{14} per sq. cm per sec. with which we are concerned. If metallic conduction is due to free electrons or electron interchange between the atoms of the metal, then some of the platinum atoms it would seem, in view of the thermal agitation, must exist for a time minus an electron. It may be that when a neutral gas molecule collides with one of these positive platinum or metal atoms, it gives up an electron even though its ionizing potential is higher than that of the metal atom.

Financial aid toward this research was given by the Executive Committee of the Graduate School of the University of Minnesota, and the author wishes to express his appreciation of this help.

Physical Laboratory,
University of Minnesota,
February 1, 1925.

[3] Langmuir and Kingdon, Proc. Royal Society **A107,** p. 61 (1925).

THE MOBILITY OF THE IONS OF THE ACTIVE DEPOSITS OF THORIUM AND RADIUM

By Henry A. Erikson

Abstract

The method used is the same as in a similar study of the active deposit of actinium.[1] As in the case of actinium, two positive active bodies differing in mobility were found in the active deposits of thorium and radium. In the case of these three deposits, all of the three swifter bodies have equal mobilities in air, and, likewise, all of the three slower bodies. The curves obtained indicate that one of the active bodies is not deposited as an A product and the other as a B product; nor is one ion atomic and the other polyatomic. It is believed, however, that one is singly and the other doubly charged.

IN an earlier paper[1] results were given showing that in the active deposit of actinium there are two positive bodies, one having a mobility of the order of 4.35 cm/sec/volt/cm and the other a mobility of 1.55.

In this paper are given the results of a similar investigation of the active deposits of thorium and radium. The method employed is similar to that used in the case of actinium.

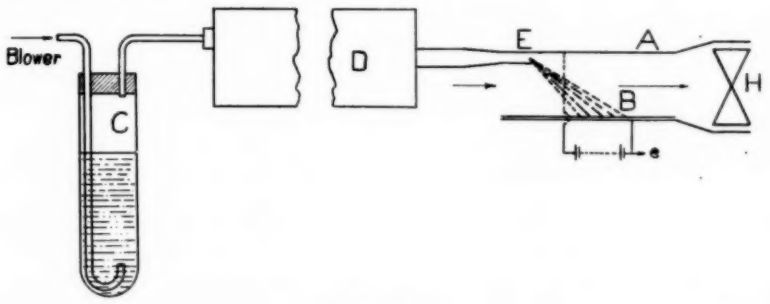

Fig. 1.

The active deposit ions were carried in a stream of air produced by the fan *H*, Fig. 1, and at *E* entered the space between two parallel plates *A* and *B* which were kept at a difference of potential of 3200 volts. The ions were then driven by the field across the air stream to the plate *B* where they were deposited. The plate *B* was removed and placed beneath an ionization chamber in the bottom of which there was a narrow slit, as shown in Fig. 2.

[1] Erikson Phys Rev. **24,** p. 622 (1924).

The rays from the active deposit passing through this slit produced an ionization current which was measured by means of a quadrant electrometer. In this way the down stream position of the different active deposits were located.

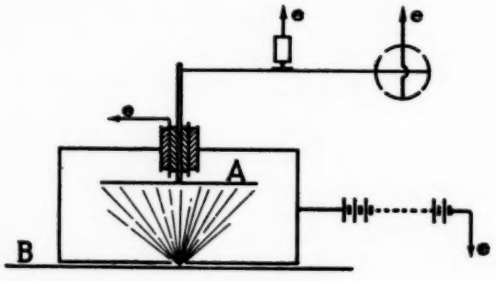

Fig. 2.

Results in the Case of Thorium Active Deposit

About 400 gm of thorium nitrate were dissolved in water and placed in a container *C*, Fig. 1. Air from a blower was forced through the

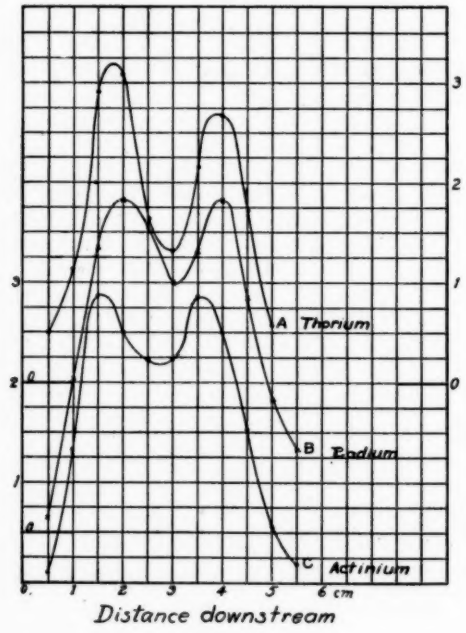

Fig. 3.

solution. The air and emanation then passed into the chamber *D*, 185 cm long and 36 cm in diameter, so large that the emanation passed through it slowly, thus permitting the formation of a greater amount of active

deposit. From this chamber the active deposit ions passed into the part of the apparatus described above. The time of exposure was one hour, and the air velocity was of the order of 10 meters a second.

The results obtained are given by curve A, Fig. 3, where the down stream distances are plotted as abscissas and the ionization currents as ordinates in arbitrary units. Curve C is for the active deposit of actinium. It is thus seen that there are two active bodies in thorium active deposit and that these have the same mobility as those of the actinium active deposit.

Results in the Case of Radium Active Deposit

The equilibrium quantity of emanation from a solution of about 3 mg of radium was collected in a test tube by displacement of mercury and

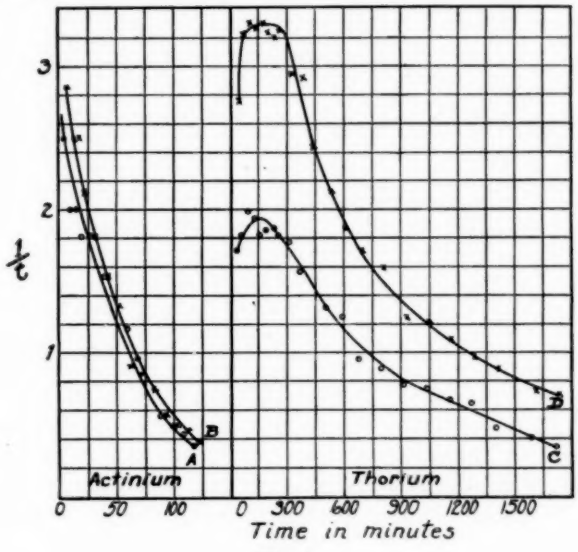

Fig. 4.

was admitted to the chamber D, Fig. 1. A length of exposure sufficient for the chamber to be emptied of the air containing the emanation was used. This interval was of the order of ten minutes. The difference of potential between the plates AB and the air velocity were the same as in the case of thorium. The results are given by curve B, Fig. 3. It is thus seen that in the case of the radium active deposit also there are two positive bodies, the same as in the case of actinium and thorium, and that their mobility values are correspondingly the same.

In Fig. 4 the decay curves for the two bodies in actinium and thorium active despoits are given. Curve A is for the more rapid of the two ions in the case of actinium and curve B is for the slower.

Curves C and D are, correspondingly, the decay curves in the case of thorium.

The half value periods deducible from these curves show that both bodies were B products at time of measurement.

Discussion of Results

In considering the nature of the two bodies, the question arises as to whether originally one came down as an A product and the other as a B product. It is, however, quite clear that this is not the case. If it were so then, owing to the short life of the A product in both the actinium and thorium series, the amount of the A product deposited should be much less. The curves in Fig. 3, however, show that about equal amounts of both are deposited.

It was also thought for a time that one of the active bodies was atomic and the other molecular in size, and that the ion of atomic size, having the greater mobility, would come down sooner. The fact, however, that an ion one atom large has the same mobility in air as an ion one polyatomic molecule large, as shown by the work on argon,[2] precludes this interpretation. The remaining alternative is that one is singly charged and the other doubly charged. An attempt to determine this by means of a magnetic field is under way. Thus far, it has not been found possible to overcome the difficulties encountered.

Financial aid toward this research was given by the Executive Committee of the Graduate School of the University of Minnesota, and the author wishes to express his appreciation of this help.

Physical Laboratory,
University of Minnesota,
July 1, 1925.

[2] Erikson, Phys. Rev. **25**, p. 890 (1925).

IONIZATION IN REACTING GASES

By A. Keith Brewer*

Abstract

Ionization associated with the oxidation of ethyl alcohol in contact with electrodes.—Previous work had shown that various gaseous reactions are accompanied by ionization. The oxidation of ethyl alcohol was chosen because of its simplicity. Nitrogen carrying 3 cc of alcohol per minute and also dry oxygen at the rate of 200 cc per minute were sent into a reaction chamber between two concentric cylindrical electrodes. The currents were measured with an electrometer provided with a radioactive shunt. Although potential differences up to 1800 volts (2400 volts per cm) were used, the current was always proportional to the voltage, being evidently far from saturation. The variation with temperature, 150° to 330°C, was exponential, increasing in the case of gold electrodes 20 fold from 200° to 320°C. With Al electrodes the current was only 1/25th as great, and chemical analysis of the products of reaction indicated that the oxidation was also greatly reduced. The results show that the reaction occurs at the electrode surfaces, the rate depending on the material and on the temperature, and that both positive and negative ions are produced. The absence of saturation is probably due to the ions being formed so close to the surface. Copper electrodes gave anomalous results, a negative Cu electrode behaving like Au while a positive Cu electrode behaved like Al. A soft glass electrode behaved like gold, except that the logarithmic increase with temperature was twice as fast for the negative as for the positive electrode.

ALTHOUGH the production of gaseous ionization by means of chemical action has received the attention of a large number of investigators since the time of Lavoisier, the problem is as yet but little understood. Richardson has pointed out the close relationship existing between this chemical effect and the photo-electric and thermionic effects, although the effects in themselves are separate and distinct.[1]

In previous papers[2,3] it has been shown that both endothermic and exothermic gaseous reactions are accompanied by ionization; that the number of ions formed is proportional to the number of molecules reacting, and that the ionic current observed is proportional to the applied voltage over the range investigated.

It is the purpose of the present paper to present evidence which will throw further light upon the production of gaseous ions by purely

*National Research Fellow.

[1] See "Emission of Electricity from Hot Bodies," by O. W. Richardson for a brief discussion of the history of the subject.

[2] A. K. Brewer and Farrington Daniels, Trans. Amer. Electrochem. Soc. **44**, 257 (1923).

[3] A. Keith Brewer, J. Am. Chem. Soc. **46**, 1403 (1924).

chemical means. Confusing complications have been reduced to a minimum by confining the study to the oxidation of ethyl alcohol vapor at temperatures well below that of ignition. There appeared to be no accompanying phenomena which could give rise to the ionization observed.

Apparatus

The apparatus used in the present research was similar to that described elsewhere.[2] Several minor improvements were added which made it possible to study the ionization in reactions even at dull red heat, and which increased the sensitivity so that currents as small as 10^{-15} amp. could be read with a reasonable degree of accuracy. The electrometer was of a modified Compton design capable of a sensitivity of over 60,000 mm per volt. The resistance of the radioactive leak, shunted across the electrometer circuit, was 2.66×10^{11} ohms. The gold electrodes were the same as those used in the previous research. Potential was supplied to the electrodes by a bank of Burgess B batteries. A copper-constantan thermocouple, enclosed in a thin walled Pyrex tube, was placed in the reaction chamber in such a manner that the temperature of either the outer, or the inner electrode, or of the reacting gas could be measured.

The Reaction

The ionization was produced by the oxidation of absolute ethyl alcohol at various temperatures below that of ignition. A stream of dry oxygen was admitted to the reaction chamber through one of the inlet tubes, while a stream of nitrogen saturated with alcohol vapor was admitted through the other. The reaction, therefore, took place between the electrodes, and in contact with only the electrodes. The oxygen supply was maintained constant at 200 cc per minute, which was far in excess of that necessary for complete oxidation of the alcohol. The rate of flow of the alcohol vapor was calculated from its vapor pressure to be 3 cc per minute.

Experimental Procedure

The ionization which resulted from the oxidation of the alcohol was observed for various electrode potentials, various temperatures of the reacting mixture, and various potential drops between the electrodes. Only one factor was varied at a time in a single set of experiments.

The procedure employed was to adjust the spot of light from the electrometer to a suitable position on the scale by means of the radioactive leak. A supply of oxygen was then admitted to the reaction

chamber through one of the inlet tubes while nitrogen was admitted through the other. No deflection of the electrometer took place. A stop cock was then turned so as to cause the nitrogen to flow through a column of alcohol before entering the reaction chamber. Any ionization that might result from bubbling was removed by passing the vapor through a long tube filled with glass wool, and heated to 200°C. Blank experiments at low temperatures showed the alcohol vapor to be free from any initial ionization. A small induction kick was always noted upon changing the gas entering the reaction chamber; this was readily distinguished from an ionization current.

Upon admitting the alcohol vapor to the reaction chamber a definite deflection of the electrometer was observed, which remained fixed as long as the temperature or the supply of reacting gases was unchanged. When the supply of alcohol was shut off the electrometer returned to the original position. If the supply of oxygen was removed while the flow of alcohol and nitrogen was kept constant, the electrometer never returned quite to the original zero. This was probably due to the fact that the reaction chamber was open at one end so small amounts of oxygen were always present.

The value of the current flowing between the electrodes was calculated by Ohm's law from the known resistance of the radioactive shunt and the voltage as given by the electrometer.

The electrometer was used under both positive and negative control, varying in sensitivity from 6,000 to 36,000 mm per volt. It was found most satisfactory to use positive control and a sensitivity of about 10,000. Since a short electrometer scale was used, the currents observed gave more than full scale deflection for all except the lower applied voltages. For larger currents the electrometer was used as a zero instrument by adjusting the radioactive leak.

The Effect of Temperature

The effect of temperature on the conductance of the reacting mixture of alcohol and oxygen, between gold electrodes, is shown in Fig. 1. The temperature given is that of the outer electrode, which is higher than that of the gas and the inner electrode. The voltage applied to the outside electrode and the supply of gas were kept constant; the temperature alone was varied. Ionization became detectable at about 150°C, and thereafter increased nearly exponentially with the temperature. For a 10° rise in temperature the conductance increased about 22 percent. The sign of the charge applied to the outer electrode changed only the

direction of the ionic current and did not effect its magnitude or the temperature at which it became detectable.

The Effect of Voltage

In Fig. 2 are given the results obtained with gold electrodes, when the supply of reacting gases is maintained constant and the mean potential gradient through the reaction chamber is varied from 0 to $\pm 2{,}400$ volts per centimeter. The observed current is directly proportional to the applied voltage, within the limits of experimental error. Although not shown on the curve, the readings were extended down to 2 volts per

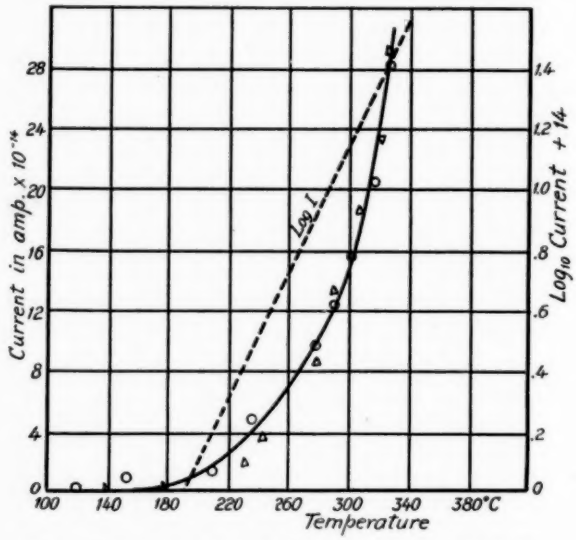

Fig. 1. Potential drop between electrodes 225 volts.
○ Outer electrode negative. △ Outer electrode positive.

centimeter potential gradient and the straight line relation was found still to hold. In these experiments the temperature of the reaction chamber was maintained as nearly constant as possible. The temperature of the gas and of the inner electrode was 200°C; that of the outer electrode was 260°C. A slight rise in temperature was always noted during the course of the reaction.

A chemical analysis of the products of the oxidation could not be made satisfactorily. However qualitative tests showed that a small amount of the alcohol was oxidized to aldehyde, to acid, and to carbon dioxide. A quantitative determination was made of the acid.

Since both positive and negative carriers are evidently formed in the reaction in practically equal amounts, it follows at once that the phe-

nomenon is ionic and not electronic. At some point during the course of the reaction the molecules involved must be broken up into positive and negative ions. In this respect the present reaction appears to differ from the reaction studied by Richardson,[4] and by Brotherton.[5] Information regarding the chemical nature of the ions and the conditions necessary for their formation was obtained by changing the material out of which the electrodes were made.

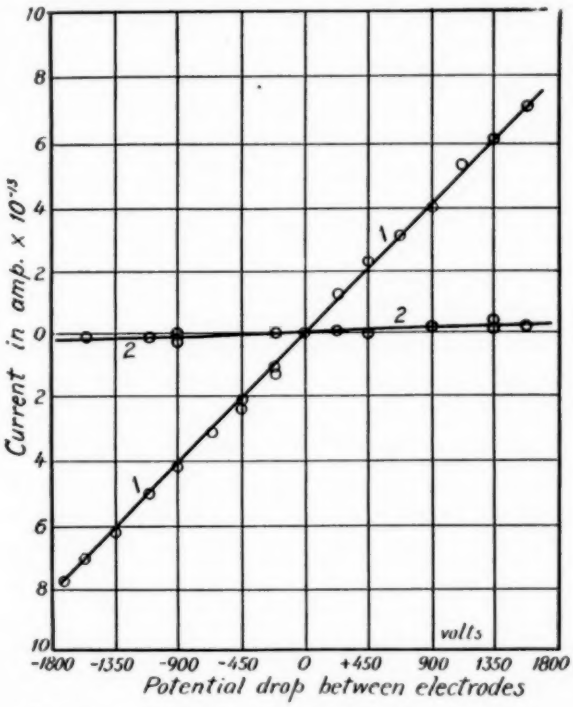

Fig. 2. 1. Gold electrodes; 2. Aluminum electrodes.

The Effect of Changing Electrode Material

Electrodes were constructed of aluminum, of copper, and of soft glass, having the same dimensions as the gold chamber. The glass outer electrode was gold sputtered on the outside to insure better electrical contact with the glass, but the reacting gases, being within the electrode, did not come in contact with the gold film. No difficulty was experienced in using the glass as an electrode for low voltages, because at the temperatures where ionization was detectable the glass was a far better conductor

[4] O. W. Richardson, Phil. Trans. **A222,** 1 (1921).

[5] M. Brotherton, Roy. Soc. Proc. **105,** 468-80 (1924).

than the reacting gas. It was impossible to use the glass at voltages higher than 900 because of electrical leakage from the supports and inlet tubes.

The experiments with the various electrodes were carried out precisely as in the case of the gold chamber. The copper electrodes had to be removed and polished at frequent intervals, because of the formation of a thick film of copper oxide on the surface.

Aluminum electrodes. The results obtained with the aluminum electrodes are shown in Fig. 2. It will be noted that for both positive and negative voltages applied the ionic current was very small, varying from 1 to 5×10^{-15} amp. Little if any rise in temperature was noted when the alcohol was admitted to the reaction chamber.

A chemical analysis of the vapors coming from the aluminum chamber showed the absence of a detectable amount of either aldehyde or acid. The aluminum oxide, therefore, does not behave as a catalyst for the oxidation of alcohol vapor.

From these results it follows that in the case of the gold electrodes the ionization observed during the reaction was not produced in the gas filled space between the electrodes but in immediate contact with the gold surface. With the aluminum electrodes the alcohol-oxygen mixture does not come in actual contact with pure metal but instead with a film of aluminum oxide covering the electrode surface. Since this insulating film of oxide is very thin the capacity between the metal on one side and the gas on the other would of necessity be very high, of the order of a farad. Therefore, if the ions were formed in the gas space between the electrodes, irrespective of the material of the electrodes, the electrometer would indicate their presence as well with the aluminum as with the gold. It would appear from this that, for the catalysis of the reaction and the production of ionization, the alcohol and oxygen must be in actual contact with a conducting surface.

The correctness of the above contention was tested by allowing ozone, which is known to decompose in the gas space, to decompose between the aluminum electrodes. An ionic current was observed almost as large as when ozone decomposed between gold electrodes.

Gold-aluminum electrodes. Since it has been found that ions are not produced from alcohol oxidation in contact with an aluminum electrode, it becomes possible, by the use of one gold and one aluminum electrode, to tell if positive and negative ions are formed in equal quantities at each electrode, and, in the case of the gold, at which electrode the ions are formed to the greater extent.

The results shown in Fig. 3 (curve 1) were obtained when the outer electrode was gold and the inner electrode aluminum. By comparison with Fig. 2 it will be seen that there is no appreciable difference in the resulting ionization, whether the inner electrode is gold or aluminum.

When the outer electrode was aluminum and the inner electrode gold only a very slight current was observed at the temperature used heretofore. When the temperature of the reaction chamber was raised so that the gold inner electrode came to the temperature of the gold outer electrode in the previous experiment, a current was again obtained about equal to that obtained when the electrodes were used in the reverse order.

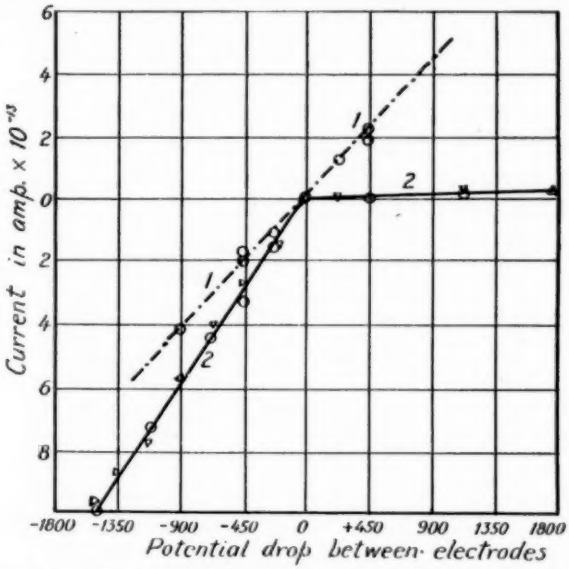

Fig. 3. 1. Gold outside—aluminum inside. 2. ○ Copper outside and inside; ▵ Copper outside—gold outside.

From these data the conclusion follows that both positive and negative ions are formed simultaneously on the same metal surface; also that the ions observed in the experiments with the gold electrodes, were formed largely on the outer electrode. The last result was to be expected, since these experiments were conducted at a temperature but slightly above that at which ionization became observable, and since at this particular temperature, there was a temperature difference between the inner and outer electrode of 60°. The fact that similar results were obtained when the inner electrode was raised to the same temperature as the gold outer electrode in the previous experiments is also interesting. Since the radius of the outer electrode is four times that of the inner, the surface exposed to the reacting gas is four times as great. But, since the

electrodes are concentric cylinders, the fall of potential around the inner electrode is four times that around the outer. The similar results, therefore, indicate that the observable ionization is proportional both to the area of the electrode and to the potential gradient at the electrode.

Copper electrodes. In Fig. 3 (curve 2) are given the results obtained with copper electrodes. It will be seen that when the outer electrode is charged negatively, the conductance through the reacting gas is but slightly larger than that obtained with the gold electrodes, but when a positive charge was placed on the outer electrode, almost no current was observed. The curve is constructed from data obtained with freshly polished surfaces. When the surface was allowed to coat over with a thick film of oxide the observed current often fell off to a quarter of the above value.

The substitution of gold or aluminum for the inner copper electrode had no appreciable effect on the currents observed. The use of an aluminum outer and a copper inner electrode gave the expected results at elevated temperatures; a current was observed when the aluminum was charged positively but none for the opposite sign.

A chemical analysis of the gases passing through the chamber showed that the quantity of alcohol oxidized fell off rapidly as the copper became coated over with oxide. Satisfactory checks were obtained only with the well coated surface, because the experiment had to be run for about ten minutes to get enough of the reacting products for a chemical test. Under these conditions only about a quarter as many molecules of alcohol were oxidized as in the case of the gold surface. The presence of a field of either sign on the outer electrode made no apparent difference in the number of molecules reacting.

The failure to detect ionization when a positive charge was placed on the outer copper electrode is not understood. It is reasonable to suppose that, since ions were present in all of the previous cases when the alcohol was being oxidized, they were also present in this case but did not become freed from the surface layer in which they were formed.

Glass-gold electrodes. In Fig. 4 is shown the current-temperature curve, taken under a potential drop of 300 volts per centimeter, when the outer electrode was glass and the inner electrode was gold. When a positive charge was placed on the glass the ionization curve was almost identical to that obtained with the gold as shown in Fig. 1 except that it began at a slightly higher temperature. For a negative charge on the glass the curve begins at a lower temperature and the logarithmic curve is almost twice as steep.

An accurate current-voltage curve could not be obtained with the glass electrode because of the unsteadiness of the electrometer at high

voltages. From the approximate data, however, it was evident that the straight line relation held as in the previous cases.

The significance of this experiment lies in showing that it is a conducting, and not necessarily a metal, surface that makes possible the escape of ions from the layer of reacting gas.

Discussion of Results

The absence of a saturation current, even at the relatively high voltages used in this research, has a possible explanation in the fact

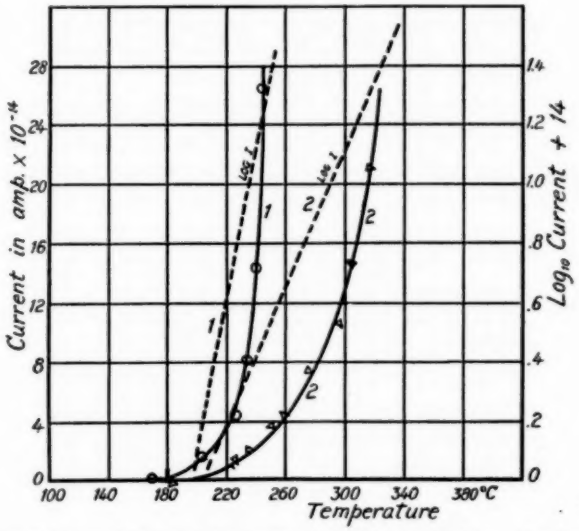

Fig. 4. Potential drop between electrodes 225 volts. 1. Glass electrode negative; 2. Glass electrode positive.

that the source of the ions is in the layer of reacting gases in immediate contact with the electrode surface.

The current observed is constituted by those ions which the field is able to draw away from the reacting layer. However, for the field to draw an ion away from a conductor, it must do so against the electrostatic image of the ion in the conductor. This image force becomes appreciable at a distance of about 10^{-4} cm from the surface. Within this distance the force increases rapidly, i.e., with the inverse square of the distance. Unfortunately, the attractive force cannot be calculated for ions within several molecular diameters of the surface due to the fact that the image forces are overlapped by the stronger molecular forces in the immediate neighborhood of the surface. However, it is reasonable to suppose that an ion at the surface would be held to the surface by a force of several million volts per centimeter.

From the above considerations it becomes apparent that any voltage capable of being used could reach but a short distance into the region in which the image force is appreciable. In fact, only those ions which had moved out to a distance of about 10^{-5} cm from the surface were detected by the highest voltages used in the present research.

If there is a rapid increase in the concentration of ions towards the surface, it would give rise to a straight line relation between current and voltage, with no appearance of saturation. A voltage sufficient to give saturation would be far above that sufficient to cause a spark. Mr. Charles F. Richter has calculated that the concentration of the ions in the layer investigated, increases approximately with the inverse cube of the distance from the surface.

It now becomes possible to suggest an hypothesis for the mechanism of ion formation. A molecule, when driven to the surface of a conductor by kinetic agitation, will be operated on both by the image force of its poles in the conductor, and by the stronger molecular force existing at the surface. (These forces will be entirely independent of any charge placed upon the conductor.) These combined forces will be comparable to the forces holding molecules together. Since the forces acting upon the molecule are electrostatic, the natural consequence is for the molecule to be broken into ions. The ions so formed are then ejected from the surface by kinetic agitation. Ordinarily, the ions, upon being driven from the surface, will recombine to reform the original molecule. Some of the ions, with larger energy content, will be shot out into the fields of other ions, with which they will combine, thus producing chemical reaction. This would explain why only a very small number of the molecules that bombard the surface react chemically.

Mr. Richter has found that if a certain critical velocity of the ions from the surface is necessary for their detection, the variation of the current with the temperature agrees qualitatively with that to be expected from Maxwell's distribution law.

Special acknowledgment is made to Dr. C. F. Burgess, of the Burgess Battery Company, Madison, Wisconsin, for the gift of fifty 45-volt radio B batteries; also to the Department of Physical Chemistry, University of Wisconsin, for the loan of the gold electrodes.

The writer is pleased to take this opportunity to thank Professor R. A. Millikan for his interest in the problem and for his many valuable suggestions.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA,
June 15, 1925.

THE PHOTO-ELECTRIC THRESHOLD FOR MERCURY

By C. B. Kazda

Abstract

In order to insure a perfectly clean surface of mercury for test, the apparatus was arranged so that carefully purified mercury flowed intermittently into a shallow iron cup and out through an overflow opening at the surface back into an electrically heated still. Direct observation showed that with such a flow the surface cleans itself of any added contamination very quickly. Also, the results for the wave-length limit were found to be independent of the rate of flow, to a rate far below that normally used, and also unaffected by the presence of gases (air, H_2, O_2, He and CO_2) and even of traces of water vapor in the photochamber. The photo-currents to a copper oxide receiver were measured by means of a quadrant electrometer to within about 1 percent for various Hg lines from a Cooper-Hewitt quartz mercury arc, correction being made for stray light by means of intermediate readings. This arc operated at 92-93 volts with 2.1 amp., was constant to 1 percent. Intensity measurements accurate to 1 percent were made by means of a vacuum thermopile connected to a d'Arsonval galvanometer (sensitivity 10^{-9} amp.) using a Hilger monochromator to disperse the light and making correction for stray light by taking readings between the lines. Plots of the ratio of corrected photo-current to corrected light intensity as a function of wave-length give the threshold at 2735A. The corresponding photo-electric work function is 4.52 volts. This result is free from the objections raised to those of previous observers and seems clearly to be the evaluation of an intrinsic property of mercury uncontaminated by surface impurities.

Introduction

FOLLOWING the early phase of discovery by Hertz,[1] Hallwachs,[2] Lenard[3] and J. J. Thomson,[4] later experimentation in the field of photo-electricity has produced a good deal of conflicting evidence regarding the conditions essential to the discharge. While no attempt will be made here to summarize these investigations it may be well, however, to state that they may be divided into two groups. To the first belong those of Fredenhagen,[5] Wiedemann and Hallwachs,[6] Kustner,[7] Hughes,[8] Sende and Simon,[9] and Suhrmann,[10] whose experiments tend

[1] Hertz, Ann. der Physik, **31,** 383 (1887).

[2] Hallwachs, Handbuch der Radiologie Vol. 3; Ann. der Physik, **33,** 301 (1888).

[3] Lenard, Ann. der Physik **2,** 359 (1900); **8,** 149 (1902).

[4] J. J. Thomson, Phil. Mag. **48,** 547 (1899).

[5] Friedenhagen, Phys. Zeits. **15,** 65 (1914).

[6] Wiedemann and Hallwachs, Ber. Deutsch. Phys. Gesell. **16,** 107 (1914).

[7] Küstner, Ann. der Physik **46,** 893 (1915).

[8] Hughes, Photo-electricity, Camb. Univ. Press, 1914 ed.; Nat. Res. Coun. Bull. **2,** No. 10 (1921).

[9] Sende and Simon, Ann. der Physik **67,** 697 (1921).

[10] Suhrmann, Ann. der Physik **67,** 43 (1922).

to throw serious doubt upon the existence of a photo-electric effect which is an intrinsic property of the material under investigation. Most of these workers conclude that the presence of impurities is an essential condition for the appearance of the photo-current. In the second group we have the investigations of Pohl and Pringsheim,[11] Piersol,[12] Millikan and his students,[13] Welo,[14] and Elster and Geitel,[15] who attribute the apparent disappearance of the photo-current to a mere shift in a long wave-length limit as a result of surface impurity. Some investigators (Koppius,[16] Tucker,[17] and others) have shown that the threshold can thus be shifted below the limits accessible to their method of observation.

In 1905 Einstein[18] made the first direct application of the quantum theory to the photo effect and suggested the following well known equation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - V_0 e$$

where $h\nu$ is the energy absorbed by the electron from the light wave, $V_0 e$ is the work necessary to free the electron from the metal, and $\frac{1}{2}mv^2$ is the energy of the emitted electron, which is measured by the product of its charge e and the potential difference V required to stop it. The validity of this relation between V and ν has been established throughout the range of visible, ultraviolet and x-ray frequencies. The value of h obtained by Millikan[19] from his photo-electric experiments, is one of the most accurate yet obtained. This equation implies that there is a photo-electric threshold characteristic of the material itself; therefore an important test of the equation is to determine whether or not such an intrinsic photo-electric threshold exists, using an experimental method which is at least free from the objections made to previous experiments.

It was decided to test carefully purified mercury running in a vacuum, for by distillation the mercury can be completely freed from gases and other impurities, and a running surface remains clean. If this should give a definite threshold frequency the matter would be settled.

The method adopted to determine the long wave-length limit was that given by Millikan.[19] The photo-currents per unit intensity were plotted against the wave-lengths used, and the curve extended until it inter-

[11] Pohl and Pringsheim, Verh. Deutsch. Phys. Gesell. **16**, 336 (1914).
[12] Piersol, Phys. Rev. **8**, 238 (1916).
[13] Millikan and students, see refs. 8, 11, 16, 17, 19, 26, 29.
[14] Welo, Phys. Rev. **12**, 251 (1918); Phil. Mag. **45**, 593 (1923).
[15] Elster and Geitel, Ann. der Physik **48**, 627 (1893); Phys. Zeits. **21**, 361 (1920).
[16] Koppius, Phys. Rev. **18**, 443 (1921).
[17] Tucker, Phys. Rev. **22**, 574 (1923).
[18] Einstein, Ann. der Physik **17**, 132 (1905).
[19] Millikan, Phys. Rev. **7**, 381 (1916).

cepted the wave-length axis. This involved first the determination of the intensity distribution of the incident light and second the measurement of the photo-current as a function of wave-length.

I. Measurement of the Energy Content of Ultraviolet Lines of the Quartz Mercury Arc

In order to get sufficient sensitivity for such intensity measurements previous experimenters have used thermopiles in air with Paschen or Thomson Galvanometers. In this work it was decided to use the type of vacuum thermopile employed by Pettit and Nicholson[20] at the Mount Wilson Observatory with a sensitivity 6 to 15 times greater, combined with a high sensitivity d'Arsonval galvanometer obtained from Leeds and Northrup. While the sensitivity (10^{-9} amp.) is only one tenth that of magnetically shielded galvanometers, the combination of vacuum thermopile and d'Arsonval galvanometer avoided the inevitable fluctua-

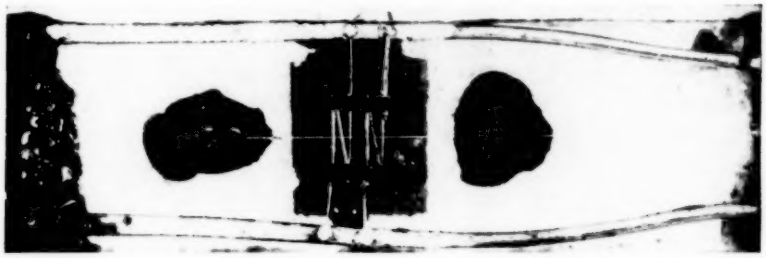

Fig. 1. Photograph of vacuum thermopile used (made by Dr. Pettit).

tions of Thomson galvanometers without loss of sensitivity. It was found necessary to suspend it by a Carman[21] suspension. The telescope was about 3 ft. and the scale about 25 ft. from the galvanometer mirror. This made it unnecessary to estimate the readings to fractions of a millimeter. All of the thermopiles used were made by Dr. Pettit at the Mount Wilson Observatory. (See the article by Pettit and Nicholson for details of construction.) The photograph shown in Fig. 1 is a three fold magnification of the last thermopile used. It will be noted that the thermopile consists of four couples connected in parallel. This thermopile gave exceedingly good results and had a high sensitivity since its resistance was nearly equal to that of the galvanometer. It is mounted upon two platinum leads which are sealed into a glass plug. A glass plate is mounted below with sealing wax and a fine glass tube is fixed upon it, to support the center of the thermopile. Directly below the couples, on the

[20] Pettit and Nicholson, Astrophysical J. **56**, 295 (1922).
[21] Carman, J. Opt. Soc. Amer. & R. S. I. **6**, 694 (1922).

glass plate, is placed a piece of fluorescing paper so as to make settings possible in the extreme ultraviolet. The couples were made of bismuth and bismuth plus 5 percent tin, while the receiver was made of tin blackened on the receiving side and placed at the junction. The couples were of the compensated type, and the double deflection was used, thus eliminating the zero reading.

It should be mentioned here that the behavior of thermocouples presumably made in the same way from the same stock of materials is not uniform. Of the considerable number of couples made, some showed drift very badly and were discarded, but those used in this work showed no drift at all and remained useful for long periods of time, reproducing results which checked very well.

As shown in the article of Pettit and Nicholson,[20] the sensitivity of the vacuum thermopile is practically constant for pressures below 10^{-4} mm. The thermopile chamber in our tests was directly connected to a two stage mercury diffusion pump, backed by a Cenco Hyvac pump. There was also a liquid air trap, just beyond the thermopile cell, when the thermopile was in operation. The pressure in the cell as measured by the McLeod gauge, was always less than 10^{-5} mm. The cell was surrounded by cotton to insure uniform temperature on all sides.

The source of light used was a Cooper-Hewitt quartz mercury arc, 100-125 volts d.c., enclosed in an asbestos lined box. The light was resolved by a Hilger monochromatic illuminator, and was then focused upon the thermopile supported inside a chamber which could be evacuated. A special carriage was made for the focusing lens which was provided with two fine screw adjustments by means of which the light could be focused on either one row of junctions or the other. By the use of both of these screw motions, a maximum reading was always obtained for each line. This accounts for the very good agreement of the individual readings obtained.

To insure constancy of operation of the mercury lamp while readings were being taken, it was necessary, in the beginning, to make a careful study of the operating conditions of the lamp. To minimize variations a resistance and reactance were connected in series with the lamp, and a 200 volt storage battery was used as source. It was found that for this lamp, when operated at 92 to 93 volts and 2.1 amp., it was possible to hold the voltage to within one volt. It might be mentioned here that it took about one hour for the lamp to reach these best conditions of operation after starting up.

The slit width used in all measurements of intensity was 20 divisions (0.5 mm) on the slit screw head of the Hilger Monochromator. Tucker[17]

made a measurement of the intensity for the same lines, but used a slit width of 25 divisions. The stray light which appears as a general background on photographic spectrum plates gave a measurable thermopile deflection. In general the minimum reading between two lines was taken as measuring stray light, except in the case of 2620 where weak lines were present (see Table I). The corrected value for the intensity for a given line was obtained by subtracting the nearest interpolated value for stray light from the observed intensity reading. The method is limited by the necessity for this correction which below 2300A becomes very large,[22] as well as by the fact that at 1900A we begin to get strong absorption by air and quartz.

TABLE I

Typical set of readings of intensity of mercury lines from quartz arc.

Wave-lengths Lines	Wave-lengths Background	Readings in mm				Average	Correction for stray	Corrected average
	2840A	14	14	14	14	14		
2804A		142	144	146	144	144	16	128
2754		43	45	44	44	44	21	23
	2725	22	23	21	22	22		
2700		56	55	56	56	56	22	34
2653		274	274	277	280	277	21	255
	(2620)	33	34	33	34	(33.5)		
2537		370	369	368	367	368	20	348
	2505	19	19	20	20	19.5		
2483		95	98	97	98	97	18	79
	2435	16	15	16	16	16		

Table I gives a representative set of readings and indicates how closely the individual readings agree. This table covers only the region of wave-lengths used in the photo-electric investigation described below. It will be noticed that down to 2483A the deviation from the average is less than 3 percent and in some other measurements, not here given, the agreement was even better.

Table II gives the average values of the deflections for three other sets of readings. These sets of readings were all taken under the same experimental conditions, the voltage across the lamp being 92 to 93 volts and the current 2.1 amp. The lamp could have run at higher temperatures to get greater intensity but the precautions that would have been necessary were not warranted since sufficiently large readings were obtained for this region of wave-lengths.

While the readings did change from time to time, it was found that over the intervals of time used in the latter part of the investigation, the readings remained practically constant. Readings taken one set after

[22] Souder, Phys. Rev. **8**, 310 (1916).

another, during the same afternoon, changed hardly at all. Over thirty sets of readings were taken.

II. Determination of the Photo-electric Long Wave-length Limit for a Clean Surface of Liquid Mercury

Extreme care was taken to obtain pure mercury. The occluded gases were completely removed by repeated distillation in an atmosphere of mercury vapor, and the photo-current was measured as soon as the fresh surface was presented to the vacuum chamber. In this way two important objections to previous experiments are removed.

Table II

Three sets of average readings for intensity of mercury lines

Wave-lengths	Uncorrected			Corrected		
	9/8/23	9/12/23	9/15/23	9/8/23	9/12/23	9/15/23
2804A	146mm	144mm	147mm	133mm	130mm	130mm
2754	45	44	46	23	22	23
2700	56	54	55	34	33	34
2653	280	276	283	257	255	260
2537	370	369	368	350	350	348
2483	97	97	97	82	80	81

After being put through the wet process, the mercury was purified by the method given by Hewlett and Minchin[23] which is the same as that used by Harkins[24] in preparing mercury for use in isotope determinations. This method consists in evaporating mercury while bubbling air through it. The mercury was then placed in a still directly connected with the photo-electric chamber. All the apparatus had previously been carefully cleaned, washed and dried and then heated for some time while being evacuated before the mercury was finally inserted. This still was made of Pyrex glass shaped like one stage of an ordinary diffusion pump, as shown in the diagrammatic sketch (Fig. 2). The still was provided with an electric heater of which the current could be varied by external resistance to regulate the rate of evaporation. The process was carried on at low pressures since the still was directly connected to the vacuum pumps.

Continuously overflowing mercury was tried, but it was observed that the center of the surface remained stationary, while the mercury flowed out at the groove from underneath. Intermittent flow, however, was found to be effective in keeping the surface clean. Rough experiments with mercury in a glass cup with a V groove in it, showed that after a

[23] Hewlett and Minchin, Phys. Rev. **21**, 388 (1905).
[24] Harkins and Mulliken, Jour. Amer. Chem. Soc. **44**, 37 (1922).

few overflowings, even the trace of oil which had been dropped on the surface could not be distinguished with a strong magnifying glass (and later a microscope). Fine dust could be observed to be drawn out through the groove from all parts of the surface. Thus intermittent overflow is a definite means for the removal of surface films which might possibly form when the surface is exposed to the chamber probably because the surface film is broken each time an overflow takes place. Intermittent overflow was automatically produced by the mercury dropping from the condenser. From the overflow the mercury returned to the still and was

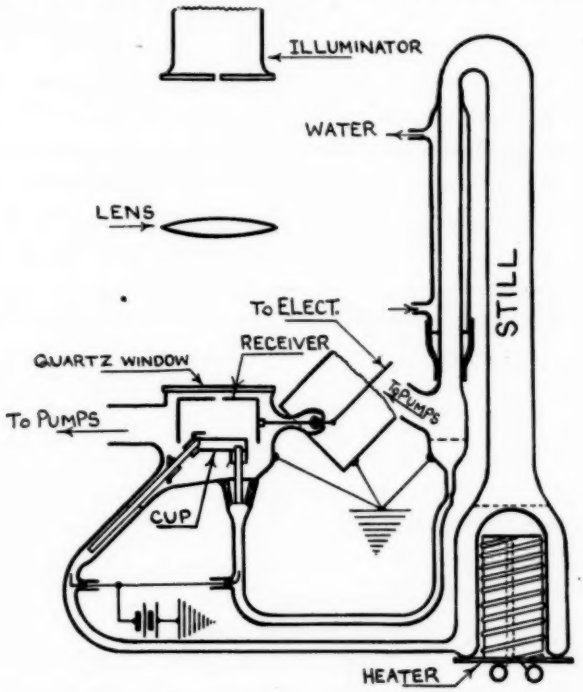

Fig. 2. Apparatus, including cup with mercury surface cleaned by intermittent overflow.

re-evaporated again. The cup itself was shallow so that a given molecule of mercury could not remain at the surface exposed to the vacuum chamber more than a second.

The attempt to take electrometer readings with overflowing mercury has been made before by McGougan[25] in connection with delta rays produced by alpha rays. Others have tried it also without success. I encountered the same difficulty as they did at first, namely, an erratic behavior of the electrometer as soon as the overflow commenced. A glass cup and vertical outlet tube was being used, and the trouble seemed to be caused by friction on the glass and by separation of the mercury into

[25] McGougan, Phys. Rev. **12**, 122 (1918).

drops. Therefore, a change was made to the iron cup and the outlet tube of iron placed at 45 degrees. The inlet tube of iron was fitted into a ground joint in the chamber, and cemented with a special high temperature cement kindly furnished by the Mantle Lamp Company of America. (This cement was also used to attach the quartz window.) While the trouble was not eliminated, it was decreased considerably. A further search was made and at last it was found that the main source of trouble was in the mercury condensation tube since a large static charge is produced when the mercury strikes the walls of the tube. So the whole condensation tube and photo chamber were closely wrapped externally by tin foil which was then grounded. The erratic behavior of the electrometer ceased entirely and results followed quickly.

The vacuum pumps were directly connected to the photo chamber and run continuously during the experiment. The pressure was read by a McLeod gauge and was never more than 10^{-5} mm. This does not include the pressure of the mercury vapor which was of the order of 10^{-3} mm at room temperature. A liquid air trap was situated near the photo chamber. Air was never introduced except through a number of drying tubes of calcium chloride and phosphorous pentoxide.

As shown in the diagram, the cup is surrounded by a copper oxide receiver. A slit in the top permits the illumination to reach the mercury in the cup. The slit is of such dimensions as not to be touched by the concentrated light from the illuminator. The same condensing lens was used as in the intensity measurements. The thermopile chamber and the photo chamber were side by side and the lateral screw motion on the holder of the condensing lens was large enough to enable the light to be focused on either chamber.

The monochromatic illuminator was mounted so that both collimator and telescope were in the same vertical plane. The lamp was mounted on a special carriage and rigidly connected to the illuminator, so that the light could be shifted from one chamber to the other by motion along a guide. This moving element being heavy was counterweighted from the ceiling so that the shift could be made easily and quickly.

The photo-current readings were made with a Cambridge and Paul Dolezalek quadrant electrometer. One pair of quadrants was grounded while the other pair was connected to the receiver. The sensitivity was 1250 mm per volt with the scale at 150 cm distance for a needle voltage of 92. The photo surface was kept sufficiently negative to ground to insure maximum readings.

The electrometer readings were taken for periods of 40 seconds or more for small currents and 8 seconds for large currents, but were all

reduced to an 8 second basis. The time interval was measured by means of a metronome which was frequently checked against a stop watch and was controlled by means of a camera shutter fitted to the outlet hole in the box containing the mercury lamp, between it and the illuminator. Correction for the electrometer leak, which was always very small and taken with each observation, was always applied to the reading. The minimum readings between lines were taken as in the intensity measurements and the same procedure was followed in correcting for stray light. This is very important here for the stray light may be composed of wave-lengths above and below that of the line itself.

As the heater on the mercury still was started at the same time as the lamp, the mercury was evaporating for some time before readings were begun. A set of intensity readings for the various wave-lengths was taken first, followed by a set of photo-current readings. Care was taken to get a maximum for each reading and three or four readings were taken for each line.

Experimental Results

Table III gives a representative set of detailed photo-current readings. The maximum deviation from average in Table III is less than 3 percent. Thus the accuracy of measurement of the photo-current is about the same as that of the light intensity.

Table III

Wave-lengths Lines	Bet. lines	Time (sec.)	Reading in mm 1	2	3	Aver.	Stray*	Correct.* av.
2804A		240	0	0	0	0	0	0
	2770A	80	0	0	0	0	0	.....
2754		80	10	10	10	1.0*	1.0	0
	2725	40	17	17	16	3.6*	3.6	.....
2700		8	12	12	12	12.0	6.2	5.8
2653		8	129	125	128	127.0	18.0	109.0
	(2620)	8	38	38	38	(38.0)		
2537		8	444	465	461	456.7	32.0	424.7
	2505	8	32	33	32	32.3	32.3	
2483		8	166	167	164	165.7	32.0	133.7
	2435	8	31	30	31	30.7	30.7	

* Reduced to a time interval of 8 sec.

No mention is made by most investigators of stray light corrections to their readings but to show the magnitude of this correction, the values are here given for both the corrected and uncorrected readings. Table IV gives the photo-current readings corresponding to the intensity measurements in Table II. The thirty sets of readings which were taken all closely check with these three sets.

In every case, a deflection was obtained for 2700A but none whatever for the much more intense line 2804A, even when exposed for several minutes. In the case of 2754A, the very small deflection obtained over a period of 40 sec. was just equal to the deflection given by the stray light for that line, so its net reading was zero. These readings were the same even when the rate of overflow was decreased somewhat. It seems certain, therefore, that the surface could not be contaminated in any way by this extremely short contact with the vacuum chamber.

TABLE IV

Wave-lengths	Uncorrected			Corrected		
	9/8/23	9/12/23	9/15/23	9/8/23	9/12/23	9/15/23
2804A	0 mm	0 mm	0 mm	0 mm	0 mm	0 mm
2754	0.8	0.7	1.0	0	0	0
2700	12.5	12.0	12.0	5.2	5.5	5.8
2652	128.0	126.0	127.0	109.0	108.0	109.0
2537	451.0	450.5	456.7	420.0	425.0	424.7
2483	165.0	164.0	165.7	135.0	132.5	133.7

As a further test, air, hydrogen, oxygen, helium and carbon dioxide were introduced into the chamber. No extended effort was made to purify them but they were very carefully dried beforehand. Under the conditions of this method *with a rapidly changing surface they were without effect upon the limit.* Even a trace of water vapor at rapid intermittent flow was without effect. These results could be reproduced at will.

As mentioned before, the long wave-length limit or threshold is obtained by plotting the photo-current per unit intensity against the wave-length or frequency, and extrapolating the curve to the intersection with the latter axis. Since the strong line 2804A gives no deflection and the much weaker line 2700A (see Table I) gives a good deflection, it is certain that the limit must fall between them.

It must be borne in mind that this intersection is governed by the points near the axis and not at all by points farther away from the axis, and therefore, it is useless to make measurements far from the axis. The curves were drawn on a large sheet of cross-section paper 20 inches wide and 40 inches long and use was made of regulation draftsmen's long flexible guides and weights and the natural position of the guides in every case governed the direction. This insures a uniform method of drawing the curves because the guides are in contact with the paper at only a few places so that the friction of the guides with the paper is small.

Since the individual curves all fall very close together, in Fig. 3 are given only the curves obtained by plotting the ratio of the final average

values of the photo-current readings and of the corresponding intensity readings, both uncorrected and corrected, against the wave-length. The individual curves, on a large scale, show a variation of plus or minus 10A for the threshold value, for both corrected and uncorrected. It will be observed that the photo-current, due to stray light, decreases rapidly as the wave-length increases beyond 2750A dropping to zero at 2770A. while the intensity reading (Table I) is still 144 mm at 2804A. This indicates that, fortunately, the stray light here is largely of longer wave-length and hence does not excite photo-emission. As a result the average curve for the uncorrected effect gives practically the same threshold value

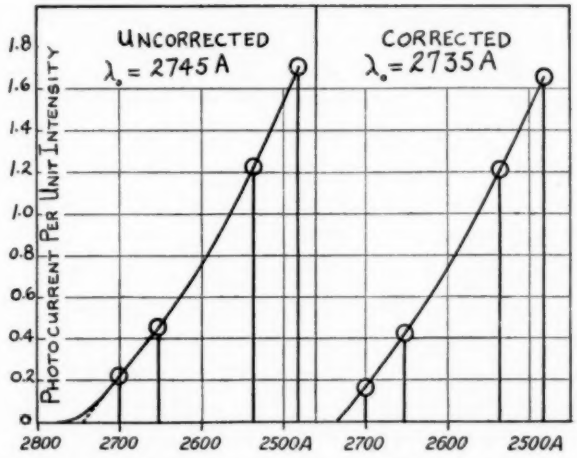

Fig. 3. Photo-current from clean mercury surface as a function of wave-length, corrected for stray light and uncorrected. Value for 2754, uncorrected, is .019.

(2745A) as the average curve for the corrected effect. Nevertheless, as emphasized by Professor Millikan,[19] to determine the threshold accurately it is important to make the correction for stray light.

Discussion

The only other data that could be found for mercury were some given by Derieux[26] and a curve by Pringsheim. Derieux states that "the drops of mercury were sensitive to line 2536A but not to line 3126A and the lines between were too weak to give any readings." The curve by Pohl and Pringsheim is given on page 76 of Hughes' book on photo-electricity. The last reading is for line 2536A. Klages[27] made an attempt to work on mercury in 1909 but does not mention the limit.

[26] Derieux, Phys. Rev. **11**, 276 (1918).
[27] Klages, Ann. der Physik **31**, 343 (1910).

Tests with water vapor showed that it has a marked effect upon *stationary mercury* even though present in extremely small amounts. The effect of a trace of water vapor at 10^{-5} mm pressure was very noticeable. *It raised the long wave-length limit. When a greater amount of water vapor was admitted the limit was pushed below the lowest value the apparatus was capable of measuring.* That a film of water vapor can exist on mercury and have a noticeable effect has also been found by Iredale[28] in connection with surface tension measurements at pressures of the order of 10^{-5} mm.

It is entirely possible that water vapor is responsible for much of the non-agreement in previous work in this field. It was also found that when once admitted water vapor is extremely hard to get rid of. However, in this experiment, as stated above, the presence of a trace of water vapor did not affect the readings *when the surface was changing rapidly.*

It seems clear that the present method for determining the threshold value for mercury is free from the chances of contamination present in previous experiments. The measurement of photocurrent at the instant a clean photosurface is presented, has not been tried before.

Millikan[29] has pointed out that the necessary conclusion from the constancy of stopping potentials is that each metal has a definite long wave-length limit and that furthermore, the photo-electric and thermionic work required to remove an electron from the surface should agree. The value of the photo-electric work function computed from the measured long wave-length limit is

$$h\nu_0 = 300\ hc/e\lambda_0 \times 10^{-8} = 12345/\lambda_0 = 4.52 \text{ volts}$$

assuming $e = 4.77 \times 10^{-10}$; $h = 6.55 \times 10^{-27}$; $c = 3 \times 10^{10}$; $\lambda_0 = 2735$A.

In conclusion, I wish to thank Professor Millikan for suggesting this work with flowing mercury and for putting the facilities of the laboratory at my disposal.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
November 20, 1923*

[28] Iredale, Phil. Mag. **45**, 1088 (1923); **48**, 177 (1924).
[29] Millikan, Phys. Rev. **18**, 236 (1921).
* Received Jan. 20, 1925; revised Aug. 20, 1925.—Ed.

THE VARIATION IN THE PHOTO-ELECTRIC EMISSION FROM PLATINUM

By Albert E. Woodruff

Abstract

Photo-electric emission from Pt.—The specimens were ribbons 3 cm by 5 mm by .013 mm thick, mounted in a Pyrex tube with a quartz window. *Effect of heat treatment on sensitivity.* Fresh specimens, cleaned with nitric acid, were insensitive to mercury arc radiation, but became sensitive when heated to moderate temperatures (250°C) by means of an electric current through them, though heating to a much higher temperature in an electric oven was without effect. Prolonged heating (17 hr) at 1300°K with pressure of 10^{-6} mm, reduces the sensitivity to light transmitted by quartz to zero. One specimen so treated remained inactive for 2 months. With pressures below 10^{-7} mm the sensitivity begins to return as soon as heating is stopped, the rate of recovery depending on the wave-length, the pressure and the previous treatment. A specimen insensitive to mercury arc radiation, was sensitive to the radiation from a tungsten filament within the tube, showing that the insensitivity is due to a shift of the threshold to short wave-lengths. *Thermionic measurements* gave an increased value for the work function φ when the threshold λ_0 was shifted to wave-lengths below that transmitted by quartz, in general agreement with the theoretical relation between φ and λ_0. At low pressures, a change of sensitivity in the ratio 1 to 7 was observed without a shift of the threshold wave-length. *Effect of electric field.* After prolonged heating at 10^{-6} mm, small electric potentials, 0.01 to 0.06 volt, are sufficient to prevent the escape of all electrons excited by mercury arc radiation. If the pressure is much lower the electric field shifts the long wave-length limit toward shorter wave-lengths. In both cases photo-activity is not restored when the retarding field is removed but only when an accelerating field is applied. The effect appears to be instantaneous. These results seem to require an adsorbed layer of gas for their explanation. However, the layer formed by heating at high temperatures seems different from that initially present in fresh specimens. This seems to be a retarding ionic layer formed from the residual gas, since at the lowest pressures this seemed to cover only patches of the surface.

Photo-electric measurements with an iron arc, in spite of fluctuations, were made possible by balancing the current against that from a standard cell illuminated by a fraction of the same light by means of a rotating prism and a variable rotating sector.

Introduction

FOR the relation of the energy of an electron emitted photo-electrically to the frequency of the incident light, Einstein has proposed the equation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - w_0 .$$

In this equation w_0 is assumed to be constant for a given substance and equal to $h\nu_0$, ν_0 being the lowest frequency of radiation that is capable of

ejecting an electron. Numerous attempts have been made to check this equation experimentally and to find ν_0 for the various substances. The experiments of Millikan and others,[1] particularly with the alkali metals, have furnished for a number of substances a value of ν_0 which appears to be characteristic of the substance. The experiments with platinum have not been so successful. Among the values first given for the long wave-length limit λ_0 for platinum corresponding to ν_0 is that obtained by Richardson and Compton:[2] viz., 2880A. Later Koppius[3] reduced this value to 2570A. He obtained the lower value simply by baking his apparatus to get rid of gases and by heating his platinum specimens. Two years later, Tucker[4] by still more severe methods of ridding his platinum specimens of gas, was able to reduce λ_0, temporarily, to a value below the shortest wave-length transmitted by quartz.

Wiedmann and Hallwachs and their students[5] working in the Physical Institute, conclude from their experiments with platinum that its photo-activity must be due almost entirely to absorbed gases and that a gas free specimen of platinum would show practically no photo-activity if excited by radiation of wave-length ordinarily used. They conclude that the action of gas upon the discharge of photo-electrons from a metal should be of two kinds; (1) an adsorbed layer of gas on the surface hinders the discharge of photo-electrons, and (2) gas absorbed in the metal assists in the process of discharge of photo-electrons. Indeed, Simon thinks that at least 99.9 percent of the photo-electrons from platinum, obtained by illumination with a quartz mercury lamp, are emitted with the assistance of absorbed gases. Hence if it were not for gases platinum would be photo-electrically inactive. According to this theory, when a metal is heated and the surface film driven off the photo-electric current should increase because the retarding influence of the surface film is removed; while more intensive heating, sufficient to drive out the absorbed gas, should reduce the photo-electric current.

A second consequence of this theory would be that the long wave-length limit should be shifted toward longer wave-lengths by the initial outgassing because of the removal of the surface layer which retards the slow moving electrons. Further outgassing, which removes the absorbed

[1] R. A. Millikan, Phys. Rev. **7**, 18 (1916); Hennings and Kadesh, Phys. Rev. **8**, 209 and 221 (1916); Sabine, Phys. Rev. **9**, 210 (1917).

[2] Richardson and Compton, Phil. Mag. **24**, 575 (1912).

[3] Koppius, Phys. Rev. **18**, 443 (1921).

[4] Tucker, Phys. Rev. **22**, 574 (1923).

[5] Wiedmann and Hallwachs, Deutsch. Phys. Ges. **16**, 107 (1914); Kober and Hallwachs, Phys. Zeits. **16**, 95 (1915); Stumpf, Deutsch. Phys. Ges. **16**, 989 (1914); Sende and Simon, Phys. Zeits. **21**, 562 (1920).

gases, should cause a return of the long wave-length limit to smaller values because the assistance of the forces of the absorbed gases is no longer present.

Suhrmann,[6] working in the laboratory mentioned above, attempted to demonstrate the truth of this theory. He tested the theory in two series of experiments, not only for photo-electric discharge of electrons but also for thermionic discharge of electrons. He used platinum and tantalum in his tests, the results of his investigations being about the same for both metals.

For platinum Suhrmann found that the long wave-length limit shifted from 2600A to 3000A and back again to 2600A as the outgassing process continued. He found that the photo-electric current excited by the wave-length 2650A decreased to a value which was only 0.17 percent of the maximum value excited by this wave-length; that excited by 2170A fell to 13.5 percent of the maximum value. Likewise the thermionic current decreased with outgassing. The value of φ in the Richardson equation was found to be 4.569 volts from the thermionic data for the outgassed condition, as compared with 4.57 volts calculated from the long wave-length limit measured at the same time that the thermionic data were taken. But the values of φ found by the two methods did not agree for the slightly outgassed condition. The value of φ corresponding to 3000A is 4.11 volts while the smallest value of φ from thermionic data is the value 4.569 volts. To account for this discrepancy Suhrmann assumes that photo-electrons come from the free electrons and that the decrease of photo-emission is determined more by the number of free electrons in the metal than by the work required to get an electron through the surface. His thermionic measurements show that the value of A in the Richardson equation, which is proportional to the number of free electrons, decreases from 4.76×10^{27} for the slightly outgassed condition to 1.7×10^{26} for continued outgassing. Suhrmann thinks that these results of his investigation confirm the theory of Wiedmann and Hallwachs.

Although the work of Suhrmann appears to confirm this theory in many respects, yet there are important experimental facts for which the theory does not account. These will be discussed later. Suhrmann's proof of the theory is based upon the assumption that photo-electrons come from free electrons. This assumption is contrary to our interpretation of the facts that photo-electric velocities are independent of temperature and that insulators are photo-active. Furthermore, the Compton effect,[7] which has been experimentally demonstrated, leaves little

[6] Suhrmann, Ann. der Phys. **67,** 43 (1922); Zeit. f. Phys. **13,** 17 (1923).

[7] A. H. Compton, Phys. Rev. **21,** 483 and 715 (1923); **22,** 409 (1923); P. A. Ross, Proc. Nat. Acad. **7,** 245 (1923); Becker et al., Phys. Rev. **23,** 763 (1924).

room for doubt that photo-electrons come from bound electrons. Suhrmann is led to make his assumption partly on account of the fact that a change in the value of φ of only 0.46 volt is not sufficient to account for the very great decrease in the photo-electric current that occurs as the metal is freed from its absorbed gas. Yet when the surface layer of gas is removed from a fresh specimen the increase in the photo-electric current is greater than the decrease from the maximum value as the specimen is outgassed. But the change in the long wave-length limit during the increase is not greater than it is during the decrease in the photo-electric current. Granting that the change in φ is not sufficient to account for the change in the photo-electric currents, how is this change brought about in the case of an increase when the absorbed gas is present? Suhrmann carried out his experiments under certain conditions and obtained these

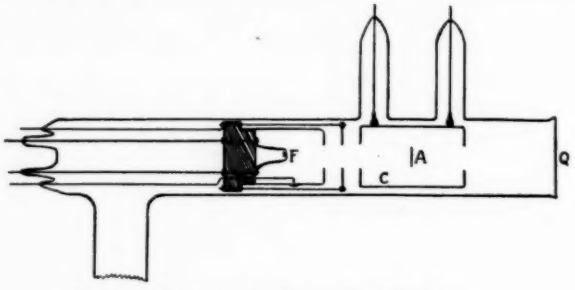

Fig. 1. Diagram of photo-electric tube.

results. Only a slight variation of the conditions would have given him quite different results. It is the purpose of the investigation reported in this paper to give results made under various conditions.

Experimental Arrangement

A photo-electric cell was made from a 40 mm Pyrex tube from which all wax and ground joints were eliminated in order to make it possible to obtain a very high vacuum. A quartz window Q (see Fig. 1) was sealed to one end of the tube with a graded seal made by the Cooper-Hewitt Electric Company. The platinum specimens A, which were ribbons 3 cm long, 0.5 cm wide, and 0.0013 cm thick, were mounted on tungsten rods sealed into glass side tubes. A copper oxide cylinder C, completely surrounded the specimen except for a hole in each end of the cylinder which allowed the incident energy to pass. The whole tube could be enclosed in an oven and baked. Mercury vapor was kept out from the experimental chamber by a liquid air trap located just outside the oven. The platinum foil could be heated by an electric current through it. The diagram shows the arrangement of the tube.

Photo-electric currents were measured with a Dolezalek electrometer which could be brought to a sensitivity of 3000 divisions per volt, if desired. Thermionic currents were measured with the electrometer or with a galvanometer. A Hilger illuminator was used for monochromatic radiation with either a mercury quartz arc, operated at constant current and constant temperature, or an iron arc as a source of radiation. A tungsten filament *F* was mounted inside the tube to provide a source of wave-lengths shorter than those transmitted by quartz.

The iron arc proved to be especially useful for short wave-lengths of monochromatic radiation. Using the mercury arc the photo-electric discharge excited by wave-lengths shorter than 2200A was so small that only under the most favorable circumstances could it be measured with any degree of accuracy. With the iron arc as a source of radiation, measureable deflections of the electrometer were obtained for exciting wave-lengths as short as 1850A. To be sure the radiation that passed the illuminator when the iron arc was the source was not strictly monochromatic. But, the radiation was of sufficient intensity so that the illuminator slits needed to be open not more than 0.5 mm. This gave a narrow range of wave-lengths sufficiently monochromatic for most purposes.

The unsteadiness of the iron arc is its chief disadvantage. The rate at which it radiates energy varies widely in a short time. This disadvantage was overcome by a null method of measurement suggested by Prof. Swann. The incident beam of radiation was interrupted by a small right angled quartz prism and reflected totally on to a comparison disk of platinum. The prism moved to and fro across the beam at right angles to it with a frequency great enough to ensure steady deflection of the electrometer. The beam of incident energy was reflected to the comparison disk as the prism crossed its path. At all other times the energy fell upon the test specimen. The comparison disk was connected to the insulated quadrant of the electrometer. Electrons discharged from the disk tended to neutralize the effect of the electrons fed into the insulated quadrant by the platinum specimen under test. By use of a rotating sector in the path of one of the beams the discharge of electrons from the test specimen was balanced against the discharge from the comparison disk. The area of the sector was adjusted until there was no deflection of the electrometer. The comparison disk received no treatment during the investigation and its photo-electric action remained constant. Since the energies incident upon the test specimen and upon the comparison disk were always of the same wave-length, a comparison of the photo-electric currents produced by them is allowable. The only assumption

involved is that the number of electrons discharged is proportional to the energy which strikes the metal. The angular area in the sector needed to balance the two photo-electric emissions is a measure of the emission from the test specimen in terms of the discharge from the comparison disk. This device was especially useful for determining the form of curves in the short wave-length region. The results obtained with the mercury arc always left doubt as to the shape of the curves in this region.

Results of Heating Fresh Specimens of Platinum

It is remarked by both Koppius[3] and Tucker[4] that the photo-electric current increases after the platinum has been heated for a time. Suhrmann[6] obtained a very large increase in the photo-electric current per unit incident energy by heating his platinum foil with an electric current. In all three cases the platinum was heated by an electric current through it, the method of heating used by most experimenters, if not by all, who have sought to get rid of gases.

An increase in photo-electric current was observed by the author when a fresh specimen was heated. All the specimens investigated were cleaned by dipping in nitric acid and by heating in a Bunsen flame. After mounting them in the tube none showed a detectable photo-emission when the total radiation from the mercury arc was focused upon them until after being heated by sending an electric current through them. It was not sufficient to heat them in the oven. In some cases the temperature of the baking process was as high as 500°C but in no case did the specimens become photo-active by heating in the oven at this temperature. Heating at a much lower temperature with an electric current through the specimen was sufficient to produce photo-activity. When the comparison disk of platinum, mentioned above, was mounted it gave very feeble emission when the total radiation from the iron arc was focused upon it. The Pyrex tube surrounding it was heated almost to the softening point but this had no effect upon the photo-emission from the disk. Photo-activity was increased by removing the disk from the tube and polishing off its surface with sand paper. It seems to be the experience of all investigators that an untreated specimen of platinum has some sort of layer, probably adsorbed gas, on its surface which hinders the escape of photo-electrons.

The following is a typical case of the behavior of a fresh specimen of platinum when an electric current is sent through it. In this case the tube was not baked but the pressure was reduced to about 10^{-6} mm. There was no emission under the influence of the total radiation from the mercury arc. Currents beginning with 0.1 amp. were sent through the specimen.

The currents were gradually increased with no observable effect until a current of 2 amp. was reached. Then the electrometer began to deflect. The current was kept constant, at 2 amp. and the observations plotted in Fig. 2 were made. (The deflections are in centimeters per 30 seconds observed at the times indicated.) The specimen could not have been heated by this current to a temperature higher than 250°C. This effect was noted many times with several different specimens. It was most pronounced for fresh specimens although it was also observed for specimens after the photo-electric emission had been reduced by prolonged heating. Increase in the photo-electric current is accompanied by a shift of the long wave-length limit toward the red.

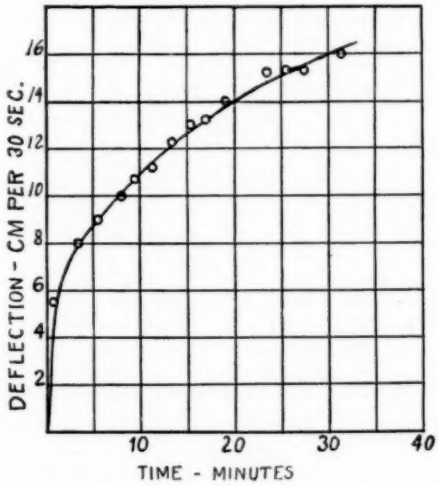

Fig. 2. Recovery of sensitivity to radiation from mercury arc while current of 2 amp. is being sent through a fresh specimen. Pressure 10^{-6} mm.

After the observations plotted in Fig. 2 were made the specimen was allowed to stand over night, the pressure being kept at about 10^{-6} mm. The next morning the rate of deflection was practically the same. When 2 amp. of heating current were sent through the specimen the deflection rose slightly to 15.3 cm. There was no further increase with time. The current was increased to 2.5 amp. and the deflection decreased. Further increase of the heating current decreased the photo-electric current gradually. When the heating current reached 4.5 amp. the deflection was but 4 cm per 30 seconds. The readings were all made with an accelerating potential of 23 volts and with the heating current flowing continuously. When the accelerating potential was reversed the specimen showed a strong discharge of positive ions coming off for heating currents greater than 2 amp. but none for heating currents of 2 amp. or less. This dis-

charge of positive ions was always found present whenever the photoelectric emission was reduced by heating the specimen.

Another specimen was tested for the same effect but in a much better vacuum. This was not a new specimen but it was newly baked to a temperature of 400°C. The pressure was below 10^{-7} mm. Beginning with 0.5 amp. the current was gradually increased to 4 amp. with no observable deflection of the electrometer. The slits of the illuminator were open 1.5 mm. At 4 amp. a slight deflection of the electrometer was observed. Readings were taken for 10 minutes. Then the slits were closed to 0.5 mm and the observations plotted in Fig. 3 were made for 2200, 2300 and 2400A. There was an accelerating potential of 14 volts. At the end of the

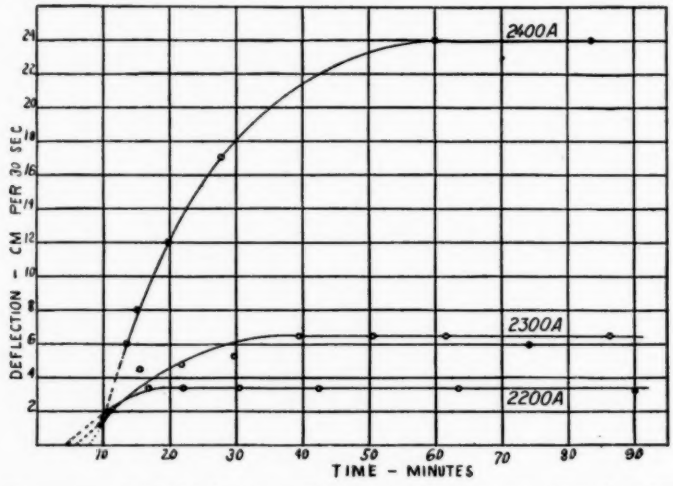

Fig. 3. Recovery of sensitivity to radiation of different wave-lengths while current of 4 amp. is being sent through specimen, previously baked at 400°C.

run the field was reversed but there were no positive ions coming off the specimen. The temperature was estimated to be about 600°C from a previous calibration curve. During the time the observations were in progress the long wave-length limit shifted from a value below that of radiation transmitted by quartz to a value of about 2550A.

The current was then increased to 4.5 amp. Immediately the photoelectric current dropped to about 80 percent of the maximum value at 4 amp. The temperature at 4.5 amp. was such that the specimen showed a just detectable faint red glow. When the current was increased to 5 amp. the emission dropped to 20 percent of the maximum value for 4 amp. Reversal of the accelerating field showed a very large emission of positive ions—much too large to be measured on the electrometer.

The Effect of Prolonged Heating on the Photo-electric Emission

One of the most pronounced effects of prolonged heating was that obtained with a specimen treated as follows: The tube was baked at 280°C for two hours. The pumps were kept running during the baking process, the pressure being about 10^{-6} mm. The specimen was then glowed 17 hours at a temperature of 1300°K. When tested for photo-electric emission there was no discharge of electrons even when the total radiation from the mercury arc was focused directly upon the specimen. This condition existed for two months. Often during this time air was admitted in to the tube to atmospheric pressure and pumped out again. Still there was no photo-emission. When the tube was filled with hydrogen and pumped out no effect was produced. Photo-activity was restored by moderate heating with an electric current.

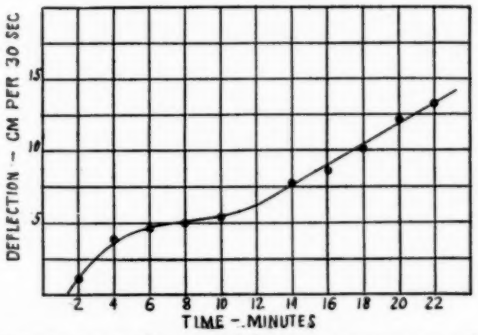

Fig. 4. Typical recovery curve for sensitivity to mercury arc radiation for specimen after prolonged heating at 1300°K. Pressure 10^{-6} mm.

The case just described is the only case in which prolonged heating caused the specimen to be inactive for such a long time. If the heating takes place at lower pressures the photo-emission disappears but returns, for the shorter wave-lengths in a few minutes, for the longer wave-lengths in a few hours at most. The time required for the return depends upon the previous history, the intensity of the heating and the duration of the heating as well as upon the wave-length of the exciting radiation and the pressure of the gas in the tube. A typical recovery curve is shown in Fig. 4. The total radiation was used for excitation. Such a curve may be repeated any number of times simply by heating the specimen for a few minutes to a moderately high temperature.

Fig. 5 shows the recovery of emission for another specimen, monochromatic radiation (2300A) being used for excitation. This specimen had been heated for 15 hours at 1300°K. The pressure during heating

was the lowest obtainable. Before the observations were begun air was admitted to a pressure of 8×10^{-6} mm. The observations were made in order beginning with the smallest heating current. The specimen was heated 5 minutes with 4 amp. of heating current (temperature about 800°K). Observations were begun as soon as the heating stopped. Immediately after the observations for the first curve were made the specimen was heated with 5 amp. (temperature about 1000°K) for 5 minutes and the observations plotted in the second curve were made. Similarly, the observations for the third curve were made after 7 amp. (temperature about 1300°K) had been used to heat the specimen. An iron arc was used as a source of radiation. The illuminator slits were open 0.5 mm. It is seen from these curves that a higher maximum is reached each time the specimen is heated. When 8 amp. were used the recovery curve was broken and irregular and after several hours the total emission had not reached the former maximum for 7 amp.

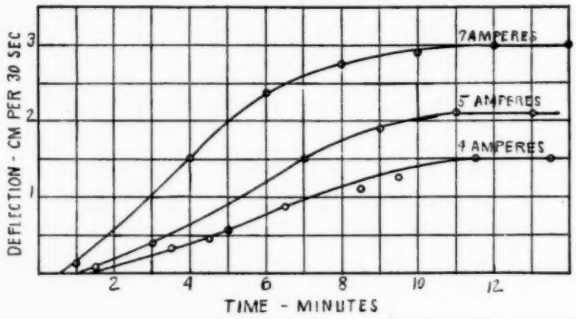

Fig. 5. Recovery of sensitivity to 2300 A (after heating for 15 hr. at 1300°K, at lowest pressure) during heating with current of 4, 5 and 7 amp. successively.

The next observations were made to test the recovery of the emission for high vacuum conditions and for different wave-lengths. The specimen last described was used. It was rebaked and allowed to cool and baked again, the pumps running during the baking, until the pressure was too low to be registered on the ionization manometer. The observations plotted in Fig. 6 were made. The process was to heat the specimen with 7 amp. of current (temperature about 1300°K) for 5 minutes, then to make the observations immediately. Two exciting wave-lengths were used, 2400 and 2200A. An observation was made for one wave-length then the monochromator was changed to the other and an observation made for it. Thus each pair of curves represents a single recovery of emission but gives the effect with the two exciting wave-lengths. The observations plotted in the three pairs of curves were made in succession, each time the specimen being heated with 7 amp. of current for 5 minutes.

It is noted that the curves do not repeat themselves but that each time the maximum approached is a little less, the order of making the curves being from (1) to (3). This behavior is different from the behavior when the pressure is high. Then the curves can be made to repeat themselves indefinitely. Aside from the fact that there is a difference in pressure it is also to be remembered that in the case where the curves repeated themselves the specimen had been heated several hours by an electric current.

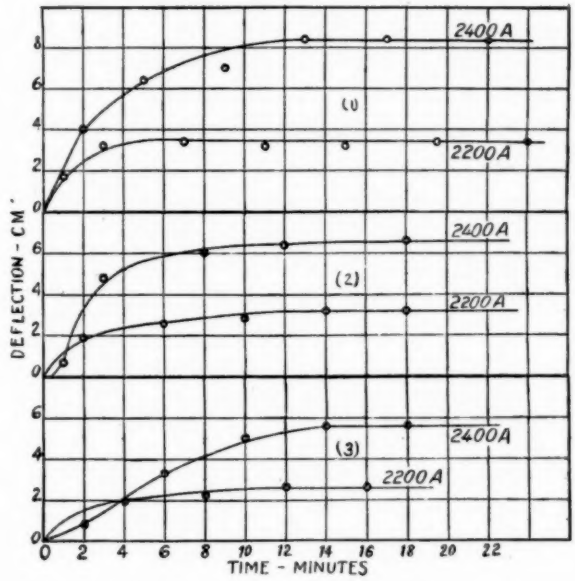

Fig. 6. Recovery of sensitivity to 2200 and 2400A, at lowest pressures, after heating to 1300°K for 5 min. The three pairs of curves were made in succession, the specimen being reheated before each pair.

The recovery curves for monochromatic radiation show that the recovery of emission occurs more rapidly for the shorter wave-lengths. This fact is emphasized particularly if the curve for the total radiation, Fig. 4 be examined. The increase in emission is still rapid after 22 minutes. Tucker[4] shows a curve plotted for a period of 2 hours in which the emission has not yet reached a maximum. The later increase in emission is that excited by the longer wave-lengths.

Still another effect of prolonged heating was observed during the latter part of the work after the best technic had been developed for obtaining a vacuum. It was found that a large change in the photo-electric current could be produced with no appreciable change in the long wave-length limit. This change in the photo-electric current was sometimes as much

as a decrease to only one seventh. This decrease in current was brought about by heating the specimen for several seconds at a temperature of about 1300°K. The emission was decreased for all wave-lengths but so far as could be detected there was no shift in the long wave-length limit. This limit was ascertained by setting the monochromator for longer and longer wave-lengths until no deflection could be observed.

The disappearance of the photo-electric emission after prolonged heating is due to the fact that the long wave-length limit has been shifted to a value below that transmitted by quartz. This was proved by mounting a tungsten filament inside the tube. The filament was properly shielded to prevent electrons getting across from it to the test specimen, being completely surrounded by a copper oxide cylinder except for an opening just large enough to allow radiation to pass. As a further precaution a copper plate was placed between the test specimen and the shield surrounding the filament. The efficiency of these devices was shown by the fact that readings taken with a magnetic field perpendicular to the line joining the filament and the test specimen agreed with those taken without the magnetic field. It was found that as the temperature of the filament was increased the radiation from it began to produce photo-emission. This test was tried on the specimen mentioned above which was so long inactive for radiation transmitted by quartz. Although there was no deflection of the electrometer under the influence of the radiation from the mercury arc, when the temperature of the filament was raised the deflection amounted to as much as 300 mm per 30 seconds.

Thermionic Measurements

Thermionic measurements were made on the specimen mentioned in the last paragraph while it was photo-electrically inactive. Before the measurements were begun the tube was newly baked out and the pressure reduced to 10^{-6} mm. The platinum foil was heated for several hours at a temperature higher than any used in the thermionic measurements. The results are plotted in Fig. 7. The value of b, in the Richardson equation, taken from this graph is 6.3×10^4. This corresponds to a long wave-length limit of 2275A if one assumes that the thermionic and photo-electric work functions are equal. After the thermionic measurements were made the specimen was still photo-electrically inactive under the influence of the total radiation from the mercury arc. However, this fact does not mean, necessarily, that the long wave-length limit of platinum was below 1850A, the shortest wave-length transmitted by quartz, for the intensity of the short wave-length energy may have been too low to give a measurable emission after the platinum had received the treatment

given it. Later investigation, using the iron arc operating on 10 to 12 amp. showed this to be the case.

Thermionic measurements were made on still another specimen. This specimen had been in use several months. It had been baked and glowed repeatedly. Before the thermionic measurements were made it had been standing under atmospheric pressure for several days. The measurements were made at as low temperatures as possible, between 1100 and 1200°K, so as to disturb as little as possible the conditions set up by the previous treatment. Currents were measured with the Dolezalek electrometer, the sensitivity being 1800 mm per volt with a capacity of about 60 cm. Just before the thermionic measurements were begun the tube was well baked and the specimen heated for two hours at a temperature of 1400°K. The pressure was kept below 10^{-7} mm.

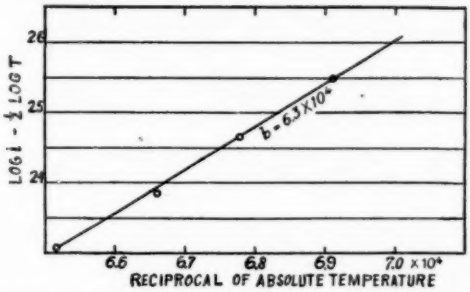

Fig. 7. Plot of thermionic measurements for photo-electrically insensitive specimen, giving value of b equal to 6.3×10^4.

The value of b as measured from the line plotted was 7.1×10^4. The specimen stood over night, the pressure remaining below 10^{-7} mm. The next morning it was glowed for one hour at a temperature of 1300°K. The thermionic measurements were repeated for the same range of temperature as the first. The value of b was 10.7×10^4. In both cases there was no photo-electric discharge of electrons immediately after the thermionic measurements were completed although the iron arc was used as the source of radiation. In the latter case photo-emission for a wave-length of 2200A was first detectable a few minutes after the heating current had been stopped. There was no emission for longer wave-lengths. The next morning the long wave-length limit had shifted toward the red so that the emission produced a deflection of 300 mm per 30 seconds for the wave-length 2400A. Other thermionic measurements at these low temperatures gave values of b abnormally high for specimens that had been heated for long periods.

These high values of b must have been due to surface conditions which were set up by the treatment given the foil. They were repeated a

sufficient number of times to ensure that they were not accidental. Each time photo-electric observations showed that there was no photo-electric emission if the foil were tested immediately after the thermionic measurements were completed. This was true even when the total radiation from the iron arc was focused on the foil. This surface condition was decidedly unstable. This is shown by the fact that if one began the measurements of thermionic current at the lowest temperature and proceeded to higher temperatures the points fell accurately on a straight line when ($\log i - \frac{1}{2} \log T$) was plotted against $1/T$, but if one returned to lower temperatures after measuring the current for higher values the points corresponding to the lower temperatures did not, in general, fall on the same line with the formerly obtained points.

Since the photo-electric long wave-length limit below 2200A could not be measured the equality of the thermionic and photo-electric work functions could not be determined. The thermionic measurements show only that whenever there is a decrease in the long wave-length limit brought about by treatment, there is a corresponding increase in the value of b of sufficient magnitude in all cases to account for the known decrease in the long wave-length limit if the equality of thermionic and photo-electric functions be assumed.

Effect of Electric Fields upon the Long Wave-Length Limit

An attempt was made to measure the velocity of the photo-electrons from a specimen that had been heated for a long period. One specimen which had been heated repeatedly was producing a deflection of 180 mm per 30 seconds with the total radiation from the mercury arc for excitation and with an accelerating potential of 30 volts. The pressure was about 10^{-6} mm. It was found that 0.06 volt was sufficient to stop all photo-electrons from the specimen. The retarding potential was increased to 2 volts. When it was removed and the specimen earthed no electrons came from the specimen when the total radiation from the mercury arc was focused upon it. When the accelerating field was reapplied the emission reappeared immediately to the full previous value. This process was repeated several times. The phenomenon was noted with several specimens. It was more pronounced with rather high pressures, that is with pressures of 10^{-5} mm, than with pressures of 10^{-7} mm, although it was present at the latter pressure. At the lower pressure there was a tendency for the specimen to remain inactive for wave-lengths above, say, 2200A. Applying an accelerating field restored the emission for the longer wave-lengths. The disappearance and restoration of the photo-

activity took place very rapidly. A double throw switch was arranged so that the change could be made from retarding field to accelerating field quite quickly. With retarding potentials as small as 0.01 volt the change could not be made rapidly enough to get a deflection of the electrometer after the retarding field was thrown on. This effect was obtained with several different specimens. It occurred only with specimens that had been heated for long periods of time, 15 to 30 hours. Tests made on unheated and slightly heated specimens did not show this effect.

Conclusion

The results of this investigation show that the initial heating of a specimen with an electric current shifts the long wave-length limit toward the red and increases the photo-electric current. This is in agreement with the results obtained by observers already quoted. The shift in the long wave-length limit and the increase in the photo-electric current may be accounted for by assuming that initially there is an adsorbed layer of gas on the surface which retards the escape of the photo-electrons. If there is such a layer of gas it may be removed by heating the platinum to a temperature of 250°C with an electric current through it. The gas is not removed by heating to 500°C in an oven. Possibly these facts may be reconciled when it is considered that all parts of the apparatus were cold when the electric current was used for heating. The gas could escape more easily than when all the apparatus was hot. Tests show that the gas discharged is not ionized.

The results of prolonged heating cannot be so readily accounted for. A first glance at the curves of Figs. 4, 5 and 6 would indicate that the Wiedmann-Hallwachs' theory is correct. Closer inspection shows that this is not the case. If the recovery of photo-activity were due to re-absorption of the gas then it should take place much more rapidly for the high pressures of Fig. 5 than for the very low pressures of Fig. 6. This is not the case. Furthermore, if the re-absorption of gas is to account for the recovery of emission the final value of the photo-electric current should depend only upon the amount of the absorbed gas. Fig. 5 shows that the final value increases as the current used to reduce the emission is raised. Fig. 6 shows that the final value is decreased as the process of heating is continued. As mentioned above, after the observations plotted in Fig. 5 were made 8 amp. were used to heat the specimen. The result was a very slow recovery which did not reach the previous maximum value after several hours. It is difficult to see how this could occur if the recovery is due to re-absorption of gas. The curves of Fig. 5 show, rather, that each time the specimen was heated more of the absorbed

and adsorbed gas was liberated. The result was an increase in the photo-electric current.

The decrease of emission to zero during the heating appears to be caused by the formation of a different sort of surface layer. The decomposition of this layer allows the photo-electric current to return, not to its former value but to a higher value which is made possible by the removal of the original gases from the surface. When 8 amp. were used as a heating current the surface layer formed was less temporary and it prevented the return of the photo-electric emission to the previous maximum value. The same sort of process is indicated by the results plotted in Fig. 6. Here as the heating is continued the final value of the photo-electric current gradually decreases. The thermionic investigation confirms these conclusions.

Further proof of the formation of some sort of retarding surface layer is furnished by the effects produced by small electric fields. An electric field could not remove or deposit, instantaneously, a layer of gas, but it could alter the arrangement of an ionic layer on the metal surface so as to make it a retarding influence.

Large decreases or increases of photo-electric current with no change in the long wave-length limit, or with insufficient change to produce the variation in the photo-electric current, may be accounted for by the formation of the retarding layer in patches on the surface of the platinum. Other areas are uncovered and continue to emit with the same or with little changed long wave-length limit. Thus the total photo-electric current is reduced but the long wave-length limit remains constant. This condition occurred in the author's investigations only when the gas pressures were the lowest. This fact would indicate that the retarding layer is formed from the residual gas in the tube. When the pressure is very low there may not be sufficient gas to form a layer which completely covers the surface of the metal.

The author wishes to acknowledge his indebtedness to the staff of Ryerson Laboratory, especially to Prof. W. F. G. Swann. It was under Prof. Swann's direction that this work was completed.

RYERSON LABORATORY,
UNIVERSITY OF CHICAGO,
January 1, 1925.

INVESTIGATION OF PHOTO-ELECTRIC VALVE COATED WITH POTASSIUM

By V. M. Albers

Abstract

Study of dumb-bell valve coated with potassium.—The tube used by Tykociner and Kunz has been studied more thoroughly. In the case of a transparent deposit on the connecting tube, curves are given showing the current through the tube when illuminated I_l, and when dark I_d. The ratio I_l/I_d reached a minimum at 40 and at 300 volts. The difference reached a maximum for a potential difference of 200 volts. The current increased linearly with light intensity at first and then less rapidly, approaching a saturation value. With an opaque film of potassium, illuminated through a window, the current increased in proportion to the voltage to 1000 volts and also in proportion to the light intensity. Evidently the thicker film gave the more efficient valve. Tests with dispersed light showed that with both transparent and opaque films, the current per unit energy decreased rapidly with increasing wave-length, reaching zero at between 520 and 540 mμ. In explanation of these effects it is suggested that photo-electric emission from the film reduces the accumulation of electrons on the wall which tends to stop the current through the tube by electrostatic repulsion. However, this does not explain the variation of the effect with wave-length.

THE purpose of this investigation was to make a thorough study of the photo-electric phenomena discovered by Professor Tykociner and Professor Kunz.[1] They discovered that an electron current passing through a tube which had a transparent film of potassium deposited on its walls, would be amplified if the tube was exposed to light. They also found that the effect was selective, the amplification depending on the wave-length as well as on the intensity of the light used to illuminate the tube.

J. M. Hyatt[2] studied the effect using visible films of potassium on the tube through which an electron current from a heated filament was passed. He found that illumination of the tube caused an increase in the current, and also that if the voltage across the tube was maintained at a constant value and the filament current increased, the current through the tube increased to a maximum and then suddenly decreased to a minimum from which it increased very slowly with increase in filament current.

[1] Tykociner and Kunz, Science **59**, 320 (April, 1924).
[2] J. M. Hyatt, Phys. Rev. **38**, 501 (April, 1924).

Apparatus

The tube used by Tykociner and Kunz was employed also in the present investigation. It consisted of two bulbs each about 5 cm in diameter, connected together by means of a tube 2 cm in diameter and 12 cm long (see Fig. 1). There was quite a heavy deposit of potassium on the inside of the bulbs and the connecting tube was treated by first depositing a film of potassium on it and then gently heating it until there was no visible film left.

The source of current through the tube was an oxide coated filament which was heated by means of a 6 volt storage battery B, and its temperature was kept constant by keeping the current, as read by the ammeter A, constant to within 0.02 ampere. The potential across the tube was furnished by dry cells for voltages below 100 volts and by a motor-generator set G for the higher voltages. The current through the tube

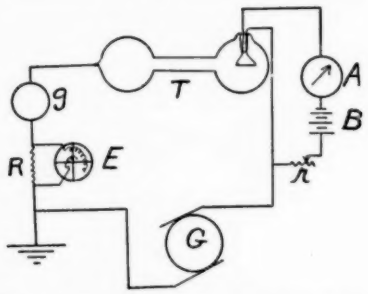

Fig. 1. The valve and the electrical connections.

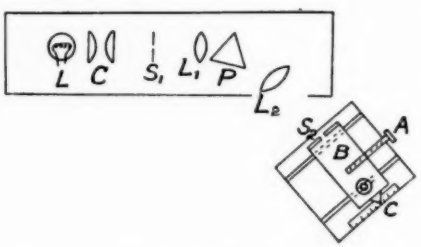

Fig. 2. The optical system.

was measured by means of the galvanometer g for the larger currents or a quadrant electrometer E for the smaller currents.

The tube was inclosed in a light tight box which had an adjustable opening, the same length as the connecting tube in the side of the box. The two bulbs were shielded, as far as possible, from the light that was used to illuminate the connecting tube. The source of light L, Fig. 2, was a 400 watt incandescent lamp which was supplied with a current of 3.7 amperes. A condenser C was so placed that it brought the light to a focus at a slit S_1 used to cut out all stray light. By means of the lenses L_1 and L_2 and the prism P the light was dispersed into a spectrum and focused on S_2. The platform B, which carried the slit and the tube, could be moved at right angles to the direction of the beam of light passing through L_2, by means of the screw A. The position of the slit could be read by means of the scale C.

A spectrometer was used to measure the wave-length of the light passing through S_2 for several different positions and the calibration curve

was plotted. A thermocouple was then fastened to the slit S_2 and readings of the deflections of the thermocouple galvanometer for corresponding positions of the slit were taken so that the curve showing the relation

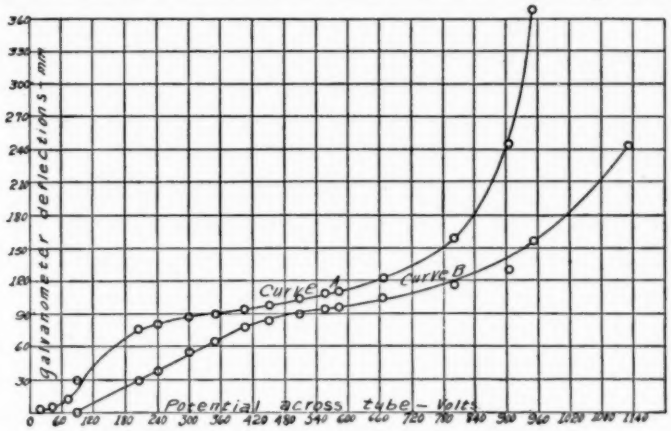

Fig. 3. Current-voltage characteristic curves when the tube is illuminated (Curve A) and when it is dark (Curve B).

between the energy passing through the slit and the wave-length of the light falling on the slit could be plotted.

Experimental Results

1. Current-voltage characteristics with a transparent film of potassium on the connecting tube were taken when the tube was dark and when it

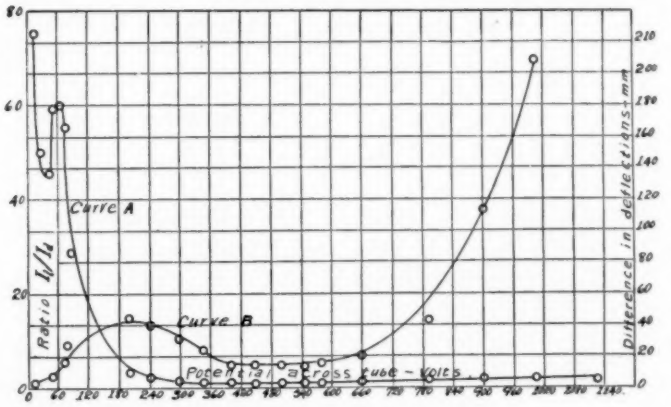

Fig. 4. Curve A shows the relation between I_l/I_d and the potential. Curve B shows the relation between ΔI due to illumination and the potential.

was illuminated (Fig. 3). From these curves the ratios of the current when the tube was illuminated I_l to the current when the tube was dark I_d were calculated for each value of the voltage (Fig. 4, curve A).

The value of the ratio was found to decrease very rapidly from zero volts to about 40 volts, then to increase very rapidly with increase in voltage for a short range and then to decrease again to a minimum value from which there was very little change. These curves changed a little in the course of time, probably because the thickness of the film of potassium in the connecting tube was continually changing, but the minimum always appeared at the same voltage. The change in the current due to illumination ΔI was also plotted as a function of the voltage (Fig. 4, curve B). When the tube was illuminated without the filament being heated no current could be detected through the tube; this shows that the increase in current when the filament is heated and the tube illuminated is not simply a photo-electric current added to the thermionic current.

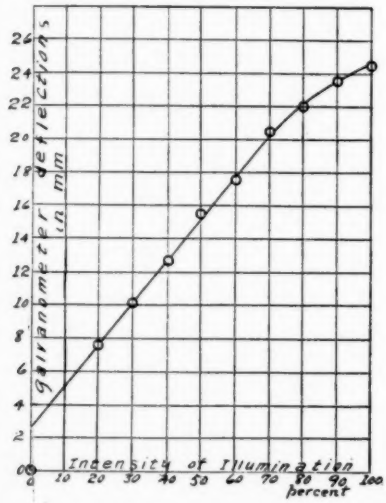

Fig. 5. Relation between the current through the tube and the light intensity.

2. In order to study the effect on the current of variation of the intensity of illumination of the tube, when the voltage was kept constant, a set of rotating sector disks was used. The maximum light intensity (no disk) was about 100 foot-candles. The light intensity was varied in steps of 10 percent each. The curves (Fig. 5) show that the current increases at first linearly with the intensity but at higher intensity bends over toward a saturation value. The results indicate that this saturation value appears for greater light intensity with low voltages than with high voltages.

It was impossible to get accurate enough data to plot curves for voltages above 200 volts because the values of ΔI were so small compared

to the value of the current through the tube when it was dark that no appreciable difference in deflection could be obtained even for a change of ten percent in the intensity of illumination.

3. In order to study the amplification produced by different wave-lengths of light, the tube was mounted vertically on the platform B (Fig. 2), far enough away from the slit (26.5 cm) so that the light which passed through the slit would illuminate the entire connecting tube.

Measurements of the increase in deflection ΔI, as read on the electrometer, were divided by E, the reading of the thermocouple galvanometer for the same position of the slit, in order to determine the increase in current per unit energy (in arbitrary units). Values of $\Delta I/E$ were found

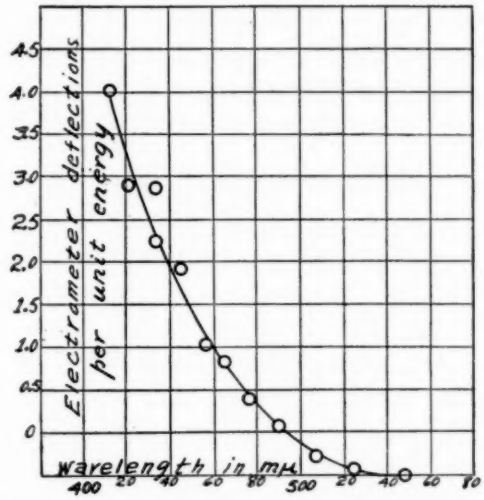

Fig. 6. Relation between the deflections per unit radiant energy and the wave-length of the light used.

for wave-lengths between 416 mμ and 550 mμ (see Fig. 6). For wave-lengths shorter than 416 mμ the amount of energy passing through the slit was too small to give an accurate calibration with the thermo-couple. The curves for different voltages and for different thicknesses of the film of potassium on the connecting tube all have the same general shape as the one shown in Fig. 6. It is interesting to notice that the curves show no maximum value for $\Delta I/E$, while an ordinary photo-electric cell has a maximum at about 440 mμ.

4. The current-voltage characteristics were taken for the same tube having a visible film of potassium on the walls of the connecting tube. This was deposited by heating one of the bulbs, which contained some

potassium. A window was then made in one side of the connecting tube by heating it at one point until the glass became clear at that point.

The same measurements were made with the tube in this condition as were made when the film was invisible except that it was impossible to measure the values of the current through the tube when it was not illuminated because it was of the same order of magnitude as the leaks in the circuit. It was also found that the current-voltage characteristics for the tube, when it was illuminated, were very nearly a straight line; in one case it was found that a straight line fits the points better than any other curve. It is interesting to notice that the tube with a visible film of potassium on its walls is a more perfect valve than the same tube with an invisible film of potassium on its walls. Also with the film of potassium thick enough to be visible no saturation value was found even for voltages as high as 1000 volts, in fact, the curves are almost straight lines.

5. The effect of the light intensity and the wave-length of the light on the current was the same as in the case of the invisible film.

Discussion of Results

In seeking an explanation for these phenomena it is suggested that, when there is a stream of electrons passing through the tube, some of the electrons would strike the sides of the tube and remain there. This would cause the walls of the tube to become charged, which would have the effect of focusing the electrons down to a narrow beam and would also decrease the effective voltage across the tube. When the walls of the tube are illuminated, the potassium, being photo-electric, will emit electons and thereby lose a part or all of this negative charge, and when this happens the two effects of the charged walls will be reduced or eliminated. The reduction of the effect of the focusing of the beam of electrons will cause the resistance of the tube to decrease which will cause an upward shifting of the current-voltage characteristic curve. The reduction of the charge on the walls of the tube will cause the repulsion of electrons back toward the filament to be decreased and this will have the same effect as an increase in voltage across the tube so it will cause a shift of the current-voltage characteristic curve toward the left. We might also try to explain these phenomena by the difference in the reflection of the electrons from the walls of the tube when they are charged and when they are uncharged.

Two interesting facts are not yet understood: (1) The distinct minimum found in the curves showing I_l/I_d plotted as a function of the voltage; and (2) the absence of a maximum at about 440 mμ in the curve

showing the relation between the wave-length of the light and the current through the tube.

ACKNOWLEDGMENTS

In conclusion, I wish to express my thanks to Professor J. Kunz, who made this work possible with his valuable help and suggestions, and to Professor A. P. Carman for the laboratory facilities which were so kindly placed at my disposal.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF ILLINOIS,
June 10, 1925.

A MATHEMATICAL TREATMENT OF THE ELECTRIC CONDUCTIVITY AND CAPACITY OF DISPERSE SYSTEMS

II. The Capacity of a Suspension of Conducting Spheroids Surrounded by a Non-Conducting Membrane for a Current of Low Frequency[1]

By Hugo Fricke

Abstract

Mathematical theory.—The following formula for the specific capacity C of the suspension, i.e., the parallel capacity of a one centimeter cube of the suspension, is derived in terms of the capacity C_0 of one cm² of the membrane surrounding the spheroids, the major axis $2q$ of a spheroid, the specific resistances r and r_1 of suspension and suspending phase, and a constant α which depends only on the axis ratio a/b of the spheroid: $C = C_0 \alpha q(1 - r_1/r)$. The values of α are given in a table. One application of the formula is the determination of the thickness of interphasial membranes (biological, adsorptive, chemical). The formula can also be used for a suspension of polarizable homogeneous spheroids when the polarization resistance is small compared to the impedance of the polarization capacity.

Introduction

In the following discussion the specific electric capacity of a disperse system is defined as that capacity which when combined in parallel with a certain resistance electrically balances one centimeter cube of the system. The present discussion applies to the case in which the capacity is due to phenomena at the interphases of the system, especially as in biological tissues, the capacity of which, as is well known, is usually very high. The capacity may be due to either or in part to each of two different causes: (1) a polarization at the interphases, and (2) the presence in the interphases of thin poorly conducting membranes which act as static condensers. The calculation presented here applies to the first case only if the polarization resistance is small compared to the impedance of the polarization capacity. The general case, when they are of the same order of magnitude, will be considered in Part III of this series of papers.

In this presentation we shall derive a formula by which we can determine from the capacity and resistance of a suspension of spheroids and their geometrical form the capacity per unit of surface of the suspended particles. One interesting application of the formula is the calculation of the thickness of the membrane when the capacity is due entirely to the

[1] For Part I, see Hugo Fricke, Phys. Rev. **24**, 575-587 (1924).

static capacity of membranes on the surface of the suspended particles. As will be shown in the following paper, this condition is probably realized for the case of blood, and, accordingly, we derive the value of about $3\times(10)^{-7}$ cm as the thickness of the membrane, which surrounds the red corpuscle, using a probable value for the dielectric constant of the membrane. This method will probably be useful also for the case of many non-biological suspensions, such as graphite suspensions, which contain well conducting particles surrounded by poorly conducting films, produced by chemical or adsorptive processes.

The fact that capacity of the type here considered is mainly dependent on the state of the interphases, makes it probable that this may be an important characteristic of the colloid properties of the system; especially may we expect this to be true for the case of biological systems. As a matter of fact, investigations which have been carried out in this laboratory have confirmed this belief. It may, for instance, be mentioned that it is found that the capacity of a tumor bears a rather constant relation to its malignancy, this relation appearing so constant that it seems probable that the measurement of the capacity may provide a very practical method for diagnosing the malignancy of a tumor.[2]

Mathematical Theory

We shall first consider the case of a suspension of particles of any form (volume concentration being ρ, and number of particles per cc being n), each particle in which is surrounded by a non-conducting membrane of uniform thickness t, and uniform dielectric constant K. The capacity of this membrane per square centimeter is $C_0=K/4\pi t)\cdot(10^{-5}/9)\mu$f. The resistance of the interior of a particle for the frequencies to be considered is supposed to be small compared with the impedance represented by the static capacity of the surface membrane. We shall call the specific conductivity of the suspending medium k_1 and of the suspension k. If furthermore, $\overline{F^2}$ is the average value of the square of the electric force in the suspending medium, we have

$$(1-\rho)k_1\overline{F^2}=k \quad V^2. \tag{18}$$

This equation expresses the fact that the heat developed in the suspension by the electric current is equal to the heat developed in a homogeneous conductor with the conductivity k for the same driving potential V. We shall now assume, following thereby in principle the method employed in Part I,[1] that the average value of electrostatic energy which is pre st at the surface of each suspended particle is obtained by placing the particle in a homogeneous field of force equal to $\sqrt{\overline{F^2}}$. Evidently this

[2] Hugo Fricke and Sterne Morse, The Electric Capacity of Tumors (in press).

electrostatic energy is proportional to C_0 and to $\overline{F^2}$, say equal to $NC_0\overline{F^2}$; consequently we have, if C is the capacity of the suspension in microfarads,

$$\tfrac{1}{2}CV^2 = n\ N\ C_0\overline{F^2}. \tag{19}$$

By Eqs. (18) and (19)

$$C = 2N\,C_0\left(\frac{k}{k_1}\right)\left(\frac{n}{1-\rho}\right) \tag{20}$$

Here N is dependent only on the constants which define the single suspended particle geometrically.

We shall now proceed to calculate N for the case of a suspension of spheroids. The electric forces in the suspending liquid are obtained by means of the equations given in Part I using $k_2 = 0$. Since the potential inside the corpuscle is constant, the resistance of the inside of the corpuscle having been assumed low as compared with the impedance of the membrane, V_{int} of Eq. (6) Part I, represents the potential difference between the two sides of the membrane. The average total static energy at the surface of a spheroid, arbitrarily placed in a homogeneous field of strength unity is consequently

$$N\,C_0 = \int_{\pi}^{0} \frac{\cos^2\varphi\, d(2\pi\cos\varphi)}{4\pi} \cdot \tfrac{1}{2}C_0 \sum\ (a \mp a,\ b,\ b) \int \frac{4x^2 dS}{(2-ab^2L_a)^2}$$

φ being the angle between the direction of the field and one of the axes of the spheroid. Hence

$$NC_0 = \frac{2}{3}C_0\left[\frac{C_a}{4M^2} + \frac{2C_b}{(2-M)^2}\right]\frac{4}{3}\pi ab^2 \cdot a \qquad (a<b)$$

$$C_a = \int (\text{over surface of spheroid } x \neq a)\left(\frac{x^2 dS}{\frac{4}{3}\pi a^2 b^2}\right)$$

$$= \frac{3}{4}\left[1 + \frac{1}{2}\left(\frac{a}{b}\right)^2\frac{1}{e^2} - \frac{1}{2}\left(\frac{a}{b}\right)^4\frac{1}{e^3}\log\frac{b}{a}(1+e)\right] \qquad (\text{when } a<b)$$

$$= \frac{3}{4}\left[1 - \frac{1}{2e^2} + \frac{1}{2}\,\frac{a}{b}\,\frac{1}{e^3}\arcsin e\right] \qquad (\text{when } a>b)$$

$$C_b = \int (\text{over surface of spheroid } x \neq b)\left(\frac{x^2 dS}{\frac{4}{3}\pi a^2 b^2}\right)$$

$$= \frac{3}{4}\left(\frac{b}{a}\right)^2\left[1 + \frac{a}{b}\,\frac{1}{e}\log\frac{b}{a}(1+e)\right] - \frac{3}{8}\left(\frac{b}{a}\right)^2 \times$$

$$\left[1 + \frac{1}{2}\left(\frac{a}{b}\right)^2\frac{1}{e^2} - \frac{1}{2}\left(\frac{a}{b}\right)^4 \cdot \log\frac{b}{a}(1+e)\right] \qquad (\text{when } a<b)$$

$$=\frac{3}{4}\left(\frac{b}{a}\right)^2\left[1+\frac{a}{b}\,\frac{1}{e}\text{arc sin } e\right]$$

$$-\frac{3}{8}\left(\frac{b}{a}\right)^2\left[1\,\frac{1}{2e^2}+\frac{1}{2}\,\frac{a}{b}\,\frac{1}{e^3}\text{arc sin } e\right] \quad (\text{when } a>b)$$

In these equations

$$e=\sqrt{1-a^2/b^2} \quad (a<b)\,; \qquad e=\sqrt{1-b^2/a^2} \quad (a>b)\,.$$

Consequently ($\frac{4}{3}\pi\, ab^2n$ being equal to ρ),

$$C=\frac{4}{3}C_0\frac{k}{k_1}\cdot\frac{\rho}{1-\rho}a\left[\frac{C_a}{4M^2}+\frac{2C_b}{(2-M)^2}\right]$$

(For the value of M see Part I, p. 581.)

By Eq. (13) ($k_2=0$): $(\rho)/(1-\rho)=(k-k_1)/\beta k$. Introducing furthermore

$$\alpha=-\tfrac{4}{3}\beta\left[\frac{C_a}{4M^2}+\frac{2C_b}{(2-M)^2}\right]\left(\frac{a}{b}\right) \qquad \text{when } a<b\,.$$

$$\text{and } \alpha=-\tfrac{4}{3}\beta\left[\frac{C_a}{4M^2}+\frac{2C_b}{(2-M)^2}\right] \qquad \text{when } a>b\,,$$

and substituting resistances (r, r_1) for conductivities (k, k_1) we obtain

$$C=\alpha\,(1-r_1/r)\;q\;C_0=C_{100}\,(1-r_1/r) \qquad (21)$$

C_{100} being the (imaginary) capacity of the 100 percent concentrated suspension, or

$$C_0=\frac{C}{\alpha q(1-r_1/r)} \qquad (22)$$

in which $2q$ represents the major axis of the spheroid. The values of α

TABLE I

Values of α as a function of b/a and of a/b.

b/a:	1	2	3	4	∞
α :	1.50	1.30	1.27	1.28	1.65
a/b:	1	2	3	4	∞
α :	1.50	1.03	0.94	0.94	$(.118\times a/b)$

are given for different values of b/a in Table I. An experimental verification of the formula will be presented in the following paper.

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CLEVELAND CLINIC FOUNDATION,
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THE ELECTRIC CAPACITY OF SUSPENSIONS OF RED CORPUSCLES OF A DOG

HUGO FRICKE

ABSTRACT

Measurements were made with a bridge, using a substitution method whereby the suspension is indirectly compared with a diluted serum which has the same specific resistance as the suspension. The bridge may be used with frequencies ranging from 800 to 4,500,000 cycles and its sensitivity is such that a capacity in parallel to 100 ohms can be measured with an accuracy of a few $\mu\mu$f at the lowest frequency. Measurements with a frequency of 87,000 cycles per sec. were made of suspensions of red corpuscles of a dog with volume concentrations between 10 and 88 percent, confirming the formula $C(\rho) = C_{100}(1 - r_1/r)$ previously derived.[1] By these measurements and the previous formula $C_0 = C_{100}/aq$ the capacity per cm² of surface of a red corpuscle is calculated to be .81μf. This capacity is independent of frequencies between 3600 and 4,500,000 cycles and is also independent of the suspending liquid. It is probably the static capacity of the membrane which surrounds the corpuscle. According to this assumption and using 3 for the dielectric constant, the thickness of the membrane is 3.3×10^{-7} cm (monomolecular).

THE following experiments illustrate the application of the theory which was presented in the preceding paper[1] and confirm it.

The capacity, which for a one centimeter cube of normal blood is of the order of a few hundred micromicrofarads in parallel with a resistance of a few hundred ohms, was measured with a specially designed bridge over a range of frequencies from 800 to 4,500,000 cycles. The sensitivity of the bridge is such that such a capacity can be measured with an accuracy of a few $\mu\mu$f at the lowest frequency. Two arms of the bridge contain a Kohlrausch slidewire which is always used near its middle point; the third arm contains a decade resistance box R_1 (General Radio Company) with a decade condenser in parallel, and the fourth arm the electrolytic cell with a variable condenser C_r (General Radio standard condenser) in parallel. By means of a switch the electrolytic cell can be replaced by a decade resistance box R_r similar to R_1. The coils in the resistance boxes are wound by the Ayrton-Perry method and their effective inductances are rather low.

The current to the bridge is delivered by an audion oscillator and the heterodyne method of detection is employed, using three stage amplification. The bridge is connected to generating and heterodyne oscillation

[1] H. Fricke, preceding paper in this issue.

and to the detector tube by very loose inductive couplings. The electrolytic cell has the form of an hour-glass with large platinized platinum electrodes sealed into the glass at the ends; it is designed to have the lowest possible amount of polarization at the electrodes. The electrode area is between 10 and 20 cm²; the distance between the electrodes between 5 and 10 cm. The cell constant is about 1. Effective stirring, which is essential, is accomplished by gently blowing through two glass tubes which are sealed to the top of the cell.

The abstract of the protocol, given in Table I, will explain the experimental procedure. The cell filled with the suspension is compared with the resistance box R_r; the difference between the settings of the condenser

TABLE I

Partial abstract of protocol for blood (11.1%)

	Units	Exp. IV$_1$		Exp. IV$_3$		Diluted serum	
R_1' (cell in)	ohms	93.3		93.2		93.1	
C_r'	arb.	6.47		6.61		8.08	
Setting of slide wire		+1		+7		−1	
R_r'' (R_r instead of cell)	ohms	93.9	93.8	93.7	93.6	93.7	93.8
C_r''	arb.	10.05	10.43	10.26	10.68	10.72	10.40
Setting of slide wire		−14.5	+7	+2.5	+24.5	0	−17.5
Temperature		23.30°	.....	23.20°	.....	22.40°	.....
$C_r''-C_r'$	$\mu\mu$f	217	240	222	247	160	141
Total inductance L	10^{-10}h	11790	11650	11480	11300	11480	11650
Equivalent capacity $(L/R_r''^2).10^2$	$\mu\mu$f	134	132	130	129	130	132
Capacity corrected for inductance	"	83	108	92	118	30	9
Corrected for difference in slide-wire setting	"	101		97		29	
Corrected for static capacity of electrolytic cell	"	95		91		21	
Capacity for cell filled with serum	"	21		21			
Capacity of blood	"	74		70			

C_r, $(C_r''-C_r')$, gives an uncorrected value for the capacity of the suspension. This value is first corrected for the inductance of the coils used in the resistance box R_r and for the difference between the inductances of the leads which connect the cell and R_r respectively to the bridge; this correction for our case is (L/R_r^2) farad, when this total inductance L is in henries. A small correction is thereafter introduced for the static capacity of the electrolytic cell, which, when filled with a homogeneous liquid of dielectric constant K, is $K/4\pi c'$ cm in which c' is the cell constant equal to the ratio of resistance to specific resistance. For the case of a suspension with a non-conducting disperse phase, like blood, K is the dielectric constant of the suspending liquid (for blood therefore about 81) and c' is the constant of the electrolytic cell c times r/r_1, r

and r_1 being the specific resistances of the suspension and the intracellular liquid. Consequently, the static capacity is $81/(4\pi c r/r_1) \times (10/9)\mu\mu f = 7.2/(cr/r_1)\,\mu\mu f$.

The value for the capacity thus obtained is still faulty, due to the difference in static coupling between the electrolytic cell and the other parts of the bridge on one side and on the other side between the resistance box R_r and the other parts of the bridge. The corresponding correction is obtained by making once for all a series of measurements with the cell filled with various dilutions of serum covering the total range of resistances used; the measured capacities are corrected as above and the values which vary very slowly with the resistance, are plotted against the resistance. From this curve a "zero value" for the capacity of the cell is found at the resistance observed in the case of blood which comprises the said difference in static coupling. This "zero value" is subtracted from the value for the capacity as obtained above.

The procedure described above would not have given a correct elimination of a polarization at the electrodes of the electrolytic cell if such an effect had been present to any appreciable amount within the experimental range of frequencies. The frequency at which the polarization becomes appreciable is easily determined by measuring the serum at decreasing frequencies; the setting of the standard condenser remains practically constant until the critical frequency is reached, when an abrupt change takes place.

A confirmation of the accuracy of this method was obtained by making measurements on cream, in which case the resulting capacity is zero. The fact that the value of the capacity of a corpuscle suspension is found to be independent of the form of the electrolytic cell and of the frequency serves as a further confirmation. (The capacity is found to be independent of the frequency between 3600 and 87,000 cycles per sec.; for higher frequencies the capacity decreases due to the fact that the impedance of the static capacity of the corpuscle membrane becomes comparable with the resistance of the corpuscle interior.)[2]

Tables II and III present the results of two series of measurements, typical of several, on the blood of a dog. They include corpuscle concentrations between 10 and 84 percent. The stated volume concentrations were derived from the resistances by an earlier formula[3] ($a/b = 1/4$). The capacity (C_{100}) for 100 percent volume concentration is calculated by formula (21) of the preceding paper.[1] The values are constant for

[2] H. Fricke and S. Morse, The electric resistance and capacity of blood for frequencies between 800 and 4,500,000 cycles, Jour. Gen. Physiol. (1925).

TABLE II

Capacity of suspensions of red corpuscles of a dog in own serum.

Defibrinated blood of dog No. 1 was concentrated by centrifugation, and the concentrated suspension was diluted with serum. Resistance r_1 of serum: 84.25 ohms; temperature: 18.95°C; constant of electrolytic cell: $c = .98$.

Frequency: 87000 cycles per sec. Date: March 22. 1925.

Experiment	Volume concentration	Resistance r	Capacity C	C_{100} (calc.)	
	(percent)	(ohms)	($\mu\mu$f)	($\mu\mu$f)	
I	83.9	931.0	374	411	Concentrated by centrifugation from original blood.
II	21.0	126.9	129	385	From 83.9 percent suspension by dilution.
III	72.0	498.	343	411	From 83.9 percent and 21 percent suspensions.
IV	47.5	230.2	237	374	From 72.0 percent suspension by dilution.
V	60.2	329.	286	385	From 83.9 percent and 47.5 percent suspensions.

TABLE III

Capacity of suspensions of red corpuscles of a dog in own serum.

Defibrinated blood of dog No. 1 was diluted with own serum. Resistance r of serum: 75.8 ohms; temperature: 23.10°C; constant of electrolytic cell: .98.

Frequency: 87000 cycles per sec. Date: March 23, 1925.

Experiment	Volume concentration	Resistance (r)	Capacity (C)	C_{100} (calc.)	
	(percent)	(ohms)	($\mu\mu$f)	($\mu\mu$f)	
I	43.9	188.7	232	388	Original blood
II	30.8	140.1	172	374	From original blood by dilution.
III	20.6	113.7	126	378	From 30.8 percent suspension by dilution.
IV	11.1	94.0	72	371	From 20.6 percent suspension by dilution.
V	10.6	93.4	74	391	From original blood by dilution.
VI	42.8	185.3	221	374	Original blood.

Average: 380$\mu\mu$f $\pm$ 2 percent

concentrations up to about 60 percent; for still higher concentrations, which approach the stage of total packing for which the theoretical foundation for the formula may be doubtful, there may be a slight tendency to an increase. Using the lower concentrations alone, we obtain $380\mu\mu f$ as the average value of C_{100}. Since the constant of the electrolytic cell is .98 (=resistance/spec. resistance), the specific value of C_{100} (corresponding to a one centimeter cube) is $380\times.98=372\ \mu\mu f$.

Using $a/b=1/4$ as in our earlier paper[3] and taking $7.2\ (10)^{-4}$ cm for the diameter $2q$ of the corpuscle, by formula (22) we obtain for the capacity per cm^2 of the membrane

$$C_0=C_{100}/aq=372\times10^{-6}/(1.28\times3.6\times10^{-4})=0.81\mu f.$$

It has been shown elsewhere[2] that the capacity of blood is independent of the frequency between 3600 and 87,000 cycles per sec. For higher frequencies the capacity decreases; this decrease, however, for the experimental range of frequencies (up to 4,500,000 cycles), is satisfactorily explained as due to the impedance of the inter- and intra-cellular liquids, with which the capacity of the corpuscle membrane is in series, C_0 itself being independent of the frequency over the above range. We find also that the capacity is not changed when the corpuscles from defibrinated blood are suspended in Ringer's solution or in an isotonic solution of dextrose.

On the ground of our present, although rather incomplete, knowledge of polarization, such a constancy of the capacity would seem hardly possible if it were due to a polarization at the surface of the red corpuscle. Furthermore,[4] there is much evidence that the resistance of the membrane which surrounds the corpuscle is high as compared with the impedance of the capacity C_0 over our whole experimental range of frequencies; therefore, even with a constant polarization capacity at the surface of the corpuscle, the observed capacity should have decreased as the frequency increased. (The resistance of the membrane may, for instance, be estimated from known data for the diffusion of electrolytes from the serium into the corpuscle.) At present, therefore, it seems probable that the observed capacity is due to the static capacity of the corpuscle membrane. The order of magnitude of the thickness of this membrane, which may be derived on this assumption, is suggestive. By using a value of 3 as the dielectric constant of the membrane (a value which of course is

[3] H. Fricke, Jour. Gen. Physiol. **6**, 741-746 (1924); Phys. Rev. **24**, 575-587 (1924), Eq. (13).

[4] H. Fricke, The electric capacity of suspensions with special reference to blood, Jour. Gen. Physiol. (1925).

rather uncertain, the more so, since the membrane appears to be monomolecular), we obtain a thickness of 3.3×10^{-7} cm. This value corresponds to a chain of from 20 to 30 carbon atoms. Thus, we evidently arrive at the conclusion that the membrane of the corpuscle is monomolecular.[4]

DEPARTMENT OF BIOPHYSICS,
CLEVELAND CLINIC FOUNDATION,
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INFLUENCE OF A BRANCH LINE UPON ACOUSTIC TRANSMISSION OF A CONDUIT

By G. W. Stewart

Abstract

General theory of transmission.—The ratio of the energy of the incident acoustic energy transmitted with the branch present to that with the branch absent is found to be

$$[(Z_1^2+Z_1\rho a/2S+Z_2^2)+(\rho a Z_2/2S)^2]\times[(Z_1+\rho a/2S)^2+Z_2^2]^{-1},$$

where the point impedance of the branch is Z_1+iZ_2, ρ is the density of the fluid, a the velocity of sound and S the area of the conduit. *Application to the Helmholtz resonator and the cylindrical resonator.* The transmission ratios found are respectively,

$$\left\{1+[4S^2(k/c-1/kv)^2]^{-1}\right\}^{-1} \text{ and } \left\{1+(4S^2)^{-1}[k/c-(\sigma\tan kl)^{-1}]^{-2}\right\}^{-1}$$

where k is 2π/wave-length, c is conductivity of the orifice, and V and σ are respectively the volume and area of the branch. The theory can be applied to ascertain the transmission, when the acoustic impedance of the side branch is known or it may be used to measure the acoustic impedance of the side branch.

Theory. This is a general treatment of the influence of the impedance in a branch line upon the transmission of acoustic energy through a conduit. Assume that the transmission occurs through a conduit of constant areas S, having one side branch and that the incident plane wave, or rather the source, is undisturbed by the action of the side branch.

The symbols used are defined as follows: k is $2\pi/(\text{wave-length})$; a, the velocity of sound; t, the time elapsed; ρ, the density of the fluid; $P=P_0e^{ikat}$, the excess pressure of the incident wave; $P'=P_0'e^{ikat}$, the actual excess pressure at the opening into the side branch; $X=X_0e^{ikat}$, the volume current (rate of volume displacement) flowing into the side branch; Z, the point impedance of the side branch, equal to $P'/\dot{X}$. The values P_0, P_0', X_0 and Z are, in general, complex.

The pressure at the junction, P', is caused by two waves, one from the source and the other from the side branch. The pressure caused by the former in the conduit is P. The pressure caused by the side branch wave can be determined very readily. Assume that the incident wave in the conduit passes from left to right. The outward volume displacement $-X$ of the wave from the branch, will, on account of symmetry be divided equally between the conduits right and left. The magnitude of the volume displacement is $X/2$ and the particle displacement is $-X/2S$ on the right and $X/2S$ on the left. The particle velocities are

correspondingly $-\dot{X}/2S$ and $\dot{X}/2S$. If the diameter of the conduit is assumed small in comparison with the wave-length, the wave produced in the conduit may be considered as plane; then the pressure produced in the conduit at the right by X is $-\rho a\dot{X}/2S$. The resulting pressure therefore is

$$P' = P - \rho a\dot{X}/2S. \tag{1}$$

Hence,
$$P'/P = 1 - \rho a\dot{X}/2PS. \tag{2}$$

Since $P'/Z = \dot{X}$, then from (1) $\dot{X}/P = 1/(Z+\rho a/2S)$, and (2) becomes

$$P'/P = 1 - \rho a/[(Z+\rho a/2S)2S]. \tag{3}$$

Let $Z = Z_1 + iZ_2$ where Z_1 and Z_2 are real. Then

$$P'/P = 1 - (\rho a/2S)[(Z_1+\rho a/2S)+iZ_2]^{-1} \tag{4}$$

and

$$(P'/P)^2 = [(Z_1^2+Z_1\rho\ a/2S+Z_2^2)^2+(\rho aZ_2/2S)^2]\ [(Z_1+\rho a/2S)^2+Z_2^2]^{-2}. \tag{5}$$

This equation, giving the value of the ratio of transmitted to incident energy in the conduit, is general and is independent of the nature of the branch. In the case of a branch in which $Z_1 = 0$, the transmission is, from Eq. (5)

$$(P'/P)^2 = [1+(\rho a/2S)^2(1/Z_2)^2]^{-1}. \tag{6}$$

Helmholtz resonator. In the case of a Helmholtz resonator as a branch, the point impedance Z is $(Mi\omega - i/\omega C)$, wherein M is the inertance of the opening and C is the capacitance of the chamber or $\rho a^2/V$, V being its volume.[1]

As shown previously,[1] the inertance of a channel is its mass divided by the square of its area. If inertance is expressed as ρ/c then c is the "conductivity." From this definition, for the channel of length L and radius R, $c = \pi R^2/L$. But "end" corrections must be made to L because the inertance is not included in the length L. Theoretically this correction is proportional to R if the channel can be regarded as in an infinite plane wall. Hence the well-known form, $c = \pi R^2/(L+\alpha R)$. With this definition of c, the point impedance is $i(\rho\omega/c - \rho a^2/V)$. Hence, $Z_1 = 0$ and Z_2 is the value in the parenthesis. Substituting in Eq. (6), the fraction transmitted is therefore

$$T = \{1+[4S^2(k/c-1/kV)^2]^{-1}\}^{-1}. \tag{7}$$

A closed tube. If a is the velocity of sound, X the volume displacement of a tube with axis in the x-direction and with constant cross-section, then the following equations hold for a simple harmonic vibration, e^{ikat},

$$\partial^2 p/\partial x^2 = -k^2 p;\ \ \partial^2\dot{X}/\partial x^2 = -k^2\dot{X}$$

[1] For a more detailed discussion see Stewart, Phys. Rev. **20**, 535 (1922), Eqs. (16) and (22).

The solutions of these equations with the additional relationship

$$\rho\partial^2\xi/\partial t^2 = -\partial p/\partial x,$$

wherein ξ is the displacement, gives the following expression

$$\dot{X} = (i\sigma/\rho a)\,(A_1 \cos kx - A_2 \sin kx)\, e^{ikat}$$

wherein σ is the area of the tube and A_1 and A_2 are pressure amplitudes. If now the tube is closed at $x=l$, $\dot{X}$ is there zero and the following relationship can finally be obtained,

$$p/\dot{X} = Z = -i\rho a/(\sigma \tan kl).$$

Thus, for a closed tube attached as a branch, $Z_1=0$ and $Z_2 = -\rho a/\sigma \tan kl$.

But no consideration has been given to the conductivity of the opening into the branch, or c, which introduces inertance as in the orifice of the Helmholtz resonator and should be added to Z_2. We then have $Z_2 = \rho\omega/c - \rho a/(\sigma \tan kl)$ and Eq. (6), or the part of the energy transmitted therefore becomes

$$T = \left\{1+(4S^2)^{-1}\left[k/c-(\sigma\tan kl)^{-1}\right]^{-2}\right\}^{-1} \tag{8}$$

Here $c=\pi R^2/(L+aR/2)$, the factor 1/2 being introduced because there is for the end of the cylinder only one-half the correction needed in the case of the orifice.

Comparison with experiment. Eqs. (7) and (8) for the transmission have been tested experimentally and found to agree satisfactorily with theory. The results will be presented in a separate paper. Experimental and theoretical results will also be given for open tubes, orifices and other branches.

Applications. The theory can be used (1) for the computation of the transmission of a conduit when the acoustic impedance of the side branch is known and (2) in the experimental determination of the acoustic impedance of a side branch. The first use is simple; the second is more complicated in practice and will be the subject of a further communication.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA,
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